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A SCHOOL CHEMISTRY

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A SCHOOL CHEMISTRY

INTENDED FOR USE IN HIGH SCHOOLS AND IN ELEMENTARY CLASSES IN COLLEGES

BY

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PREFACE

An occasional visitor to the ordinary public lecture on chemistry, whose eyes have been dazzled by a display of fireworks, regards the subject as most interesting and fascinating, and supposes that the chemist's life is spent amid a continuous round of brilliant pyrotechnics. The student, whether at school or college, takes quite another view of the matter, and very frequently considers chemistry one of the most difficult subjects of his course. He meets a large number of new facts which unfortunately seem unconnected with ordinary daily life. The idea is soon formed that chemistry is a thing apart, that it forms a realm by itself, presided over by a special god or goddess, — a deity, alas, difficult to appease and propitiate, the secrets of whose kingdom are most grudgingly revealed.

Not only are new facts met with, but new theories are encountered, and the theories do not seem to arise from the facts. If any connection is regarded as existing between the two, the theories are supposed to be the more fundamental, the facts striving, if possible, to correspond with them. To many young students it would be matter of surprise that chemistry does not hang upon the atomic theory, that a number of the most brilliant and epoch-making discoveries were made without its assistance, that analyses were carried on and manufactures engaged in before the theory was enunciated, and that without the experimental basis provided by research, the atomic theory would be of no more value than the unfruit-

ful hypothesis of Democritus. The beginner is liable to consider that he has made great advance when he has learned to call water H_2O, though the probability is that he has no idea why the formula is given, and has very vague notions as to its real meaning and significance.

The endeavour is made in this little book to help the pupil in the discovery of new facts, to enable him to see their connections, and to show how facts lead to theory, and theory aids in investigation and in the discovery of further facts. The subject is presented in what seems to me the correct perspective, theory being subordinated to fact.

The order in which the various topics are taken up appears to me to be the most simple. Water is first discussed, as being one of the most common substances, and one with whose properties the pupil is already somewhat familiar. Thereafter follows the consideration of hydrogen and oxygen, the latter leading up to the study of air and its constituents. Throughout the book the arrangement is equally simple. Definitions are brought in as they are needed and as they arise from consideration of the facts investigated. No mention of the atomic theory is introduced until the study of a large number of facts has afforded an intelligible basis for it, until, indeed, the pupil has in his possession most of the facts upon which Dalton founded the theory. He is thus enabled to obtain an accurate view of the real meaning of formulæ and an ability to use them correctly.

One of the difficulties of many students in the continued pursuit of chemistry after leaving school is that they have to unlearn a good many things that they have learned (or mislearned) in their early study. It is hoped that the student of this book will have no such experience, but that he will have laid a thoroughly solid foundation with no crumbling stones

nor untempered mortar. Though the modern theory of electrolytic dissociation has not been introduced, since I do not think it advisable in an elementary book of this character, I trust that few statements will be found at variance with the most recently discovered facts. I have endeavoured to make any description of industrial processes up to date, and not to describe obsolete processes as though actually employed at the present day. As an example, I may mention the electrolytic production of sodium which has entirely superseded the reduction of the carbonate by carbon, and even the later process of reduction of the hydroxide by iron and carbon.

I trust that the book will not only prove valuable to the pupil taking up chemistry with a view to further study of the subject, but that it will be found preëminently useful from an educational point of view. The interrogatory method is largely employed; the questions though for the most part simple are intended to stimulate thought, being calculated to make the pupil observe the important phenomena, to see their connections, and to understand their full significance. It is hoped that in this respect the book will prove itself superior to most of the text-books on chemistry written for high school and college use.

The experiments are spoken of as though performed by the pupil, but where this is not feasible he will be able to follow the experiments of the teacher, to whose judgment is left the decision which experiments to do himself and which to leave to the pupil. In fully equipped schools the experiments may all be done by the pupil, but in some schools it might be inconvenient to provide many sets of apparatus for the electrolysis of water, for instance.

I have had considerable experience in teaching beginners in chemistry, both dull and clever, and have found that the diffi-

culties encountered by each class are very similar, the difference being mainly that the clever ones can be more easily helped to overcome their difficulties.

My experience as a teacher has been widened by experience as an examiner. Within two years I examined over three thousand papers in chemistry, written by pupils from a great number of schools, and it was largely owing to my experience as an examiner that I was led to prepare this book, which I trust will commend itself to many teachers throughout the country.

While I am indebted to a number of friends for suggestions in the treatment of particular points, I wish to mention especially the help given me by Mr. Frank Rollins, A.B., of the Peter Cooper High School of New York City. From the time that my project began to take shape I have been greatly helped by Mr. Rollins's criticisms and suggestions, and have been encouraged by his kindly interest in the work.

J. W.

OCTOBER, 1900.

PREFACE TO THE SECOND EDITION

THE favourable reviews of the first edition that have appeared in scientific and educational periodicals, and the experience of teachers and students, indicate that the method in which the subject-matter has been treated commends itself to those for whom the book is intended. In bringing out the second edition I have not thought it advisable to make any very sweeping changes, but, being more convinced than ever that the atomic theory should be relegated to a subordinate place, I have added Appendix B on the law of reciprocal proportions, showing how numbers that are practically atomic weights may be arrived at without introducing the idea of atoms. I strongly advise all readers to study this appendix carefully before passing page 75. Appendix C has a similar object. I have introduced a third appendix on electrolytic dissociation, not because I think the subject specially suited to an elementary book, but because the syllabus in many schools includes it. I have tried to present the essentials of the theory as simply as possible.

There have been in recent years no very startling discoveries in the domain of elementary chemistry, nothing similar to the liquefaction of air and the discovery of argon. The epoch-making work on radioactivity belongs to a higher branch of the subject. There have been, however, notable advances in industrial chemistry which have found a place in this edition. *Very prominent are the development of the sulphur industry* in Louisiana and the electrical manufacture of nitric acid from

the air. This latter is likely to be of immense importance because there has been practically only one source of nitric acid and nitrates; namely, Chile saltpetre, an impure sodium nitrate. The demand for sodium nitrate as a fertiliser has grown considerably of late years and will continue to grow, while the deposit in Chile is far from inexhaustible. Much remains to be done to make the artificial production of nitric acid a complete success. A process used for eighteen months at Niagara was abandoned, but another now employed in Norway seems likely to succeed.

The table of atomic weights has been changed to give the latest figures, and the most recently determined gramme-molecular volume has been adopted. It is hoped that nothing out of date has been retained in the book and that it will be found to meet the wants of increasing numbers of teachers and pupils.

CONTENTS

SET OF CHEMICALS FOR TEN PUPILS

5 lbs. Ammon. Chloride, commercial.
3 " " Nitrate.
½ lb. " Bromide.
3 oz. " Iodide.
¼ lb. Antimony metal.
¼ " Arsenic powder metal.
1 " Arsenic Trioxide, powdered.
1 " Barium Chloride cryst.
1 " Bone-black.
1 " Bromine.
2 lbs. Carbon Bisulphide.
1 lb. Calcium Chloride, dry and bottle.
2 lbs. Calcium Oxide, and bottle.
½ lb. Copper Wire, naked.
1 " " Sulphate cryst.
3 lbs. " Turnings.
1 lb. Ferrous Sulphate, commercial.
3 lbs. " Sulphide.
1 lb. Gypsum.
3 oz. Iodine.
1 " Litmus.
2 large sheets each red and blue Litmus.
1 lb. Lead Nitrate.
3 lbs. Manganese Dioxide for Chlorine.
2 " Marble.
5 " Mercury.
½ lb. Mercuric Oxide, red.
3 lbs. Oxalic Acid.
1 lb. Paraffin.
2 oz. Phosphorus.
¼ " Potassium, metal.
1 lb. " Bromide.
2 lbs. " Chloride.

¼ lb. Potassium Iodide.
1 " Caustic Potash pure white sticks.
2 lbs. Potassium Chlorate.
¼ lb. " ferrocyanide.
2 lbs. " Nitrate cryst.
½ lb. Potass. Permanganate.
2 ft. Platinum Wire for flame colours.
1 lb. Potassium bichromate.
½ " Sodium metal.
5 lbs. " Carbonate, dry.
1 lb. Caustic Soda, purified, in sticks.
1 " Sodium Nitrate.
½ " " Bromide.
2 oz. " Iodide.
1 lb. " Phosphate.
¼ " " Biphosphate.
½ " Strontium Chloride.
5 lbs. Sulphur, in rolls or flowers.
1 lb. Tin, granulated, pure.
5 lbs. Zinc, "

LIST OF CHEMICAL APPARATUS REQUIRED FOR EACH PUPIL

1 lb. Glass Tubing, assorted sizes.
3 Bulb Tubes.
1 U Tube.
½ doz. Test-tubes, 4 in. × ½.
1 " " 6 " × ¾.
2 Ignition Tubes of hard glass, test-tube shape.
6 ft. Black Rubber Tubing for connecting apparatus.
1 Rubber Cork, with two holes, to fit large flask.
5 doz. Corks, assorted sizes.
3 Cork Borers.
1 Flask, 500 cc.
1 " 200 cc.
1 " Erlenmeyer, 200 cc.
1 " " 300 cc.
1 Deflagrating Spoon.
1 Triangular File, 5 in.

1 Round File, 5 in.
1 Nest Beakers, 50 cc. to 400 cc. approx.
1 Evaporating Dish, 3 oz.
1 " " 6½ oz.
Filter Paper, 1 package 3 in., 1 package 4 in.
1 Funnel for each size of paper.
1 Thistle Tube, 10 in.; 1 Tube, 15 in.
1 Retort Stand, medium size, 2 rings and 1 clamp.
1 Sand Bath, 6 in.
1 Alcohol Lamp, 8 oz., or Bunsen Burner with rubber tube.
Tapers.
1 Test-tube Brush.
1 " Support.
1 square Wire Gauze, 5 in.
1 Thermometer, graduated to 150° C.
2 Burettes, 50 cc., graduated $\frac{1}{10}$, with pinchcock.
3 Watch Glasses.
1 Lime Tower.

The price of apparatus and of chemicals may vary, but the above sets cost approximately $12.00 for the apparatus and $25.00 for the chemicals, exclusive of freight.

I would recommend Messrs. Eimer & Amend of New York and Messrs. E. H. Sargent & Co., 106 Wabash Avenue, Chicago, as reliable dealers, and they will supply the goods if asked for Waddell's set of apparatus or Waddell's set of chemicals. Canadians are recommended to purchase direct from Messrs. Lyman Sons & Co., Montreal, and to specify in their order for apparatus or chemicals that the goods are to be supplied in accordance with the list in Waddell's School Chemistry.

The set of chemicals for ten pupils may with care suffice for double that number.

It is assumed that large apparatus, such as balances and electric batteries, will be in the laboratory, as also such heavy chemicals as acids and alcohol, and hence these things are not given in the lists.

CHEMISTRY

CHAPTER I

WATER

The Freezing of Water. — EXPERIMENT 1. Into three separate test-tubes, or open dishes, such as cups, pour some rain-water, well-water, and sea-water (or, failing that, water with a little salt in it). Is there any difference in taste? Now, cause some ice to form, either by putting the dishes out of doors (if the weather is cold enough) or by surrounding them with a mixture of ice and salt, such as is used in making ice-cream. If the ice is formed in an open dish, it will probably be sufficient to wash off a solid piece of it, but if formed in a test-tube,

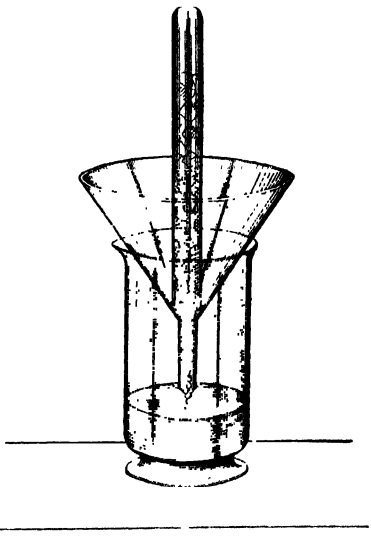


FIG. 1

surrounded by a freezing mixture, it will be best to remove the test-tube from the freezing mixture as soon as

there is a considerable quantity of ice formed in it, to invert the test-tube over a funnel, as shown in the figure (Fig. 1), to allow the water to drain off, and then to let about one-half or two-thirds of the ice melt without being disturbed. Remove the ice to a clean dish; melt it, and taste. How does the taste compare with that of the water from which the ice was formed? Does the salt-water ice taste salt? Is the water produced by melting the ice more or less pure than the water in which the ice was formed?

EXPERIMENT 2. Add to some water a grain or two of potassium permanganate (used in Condy's disinfecting fluid). What is the colour of the water? Let ice be formed as in the first experiment. Is the ice coloured like the water? Does it taste like the water?*

What is one way of getting moderately pure water from an impure water?

The Distillation of Water. — A better way of obtaining pure water is to boil any ordinary water and to cool the steam that comes off from it in such a manner that the water formed from the steam may be collected. This process is called *distillation*, and the water so obtained is called *distilled water*.

* When told to taste anything, always be very careful, unless you are perfectly familiar with the nature of the substance. It is a good plan to dip the finger into the liquid and to touch the finger to the tongue. In case you find the taste is very slight, you may then take more, unless you are warned to be careful. In the present case, for instance, it will depend on how much permanganate has been used whether you will be able to detect its taste in a drop of the water, or may need to take a teaspoonful. In tasting a solid, merely touch a little crystal to the tongue, using just enough to distinguish the taste. It is always well in your chemical experiments to avoid swallowing anything until you are quite sure that it is harmless. Be also very careful in smelling.

EXPERIMENT 3. Fit into a thin flask holding about half a litre (nearly a pint) a cork with a hole through which a long glass tube, bent as in Fig. 2, passes tightly. Half fill the flask with salt water, put in the cork, and heat the flask. The figure shows a piece of apparatus called a retort stand, intended for holding vessels to be heated. It also shows how the flask is held in position.

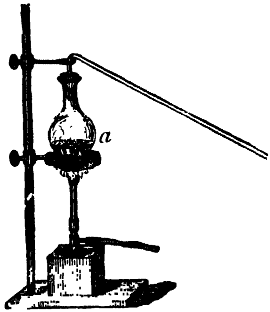


FIG. 2

When the water in the flask boils, what do you see in the tube? When the tube is all quite hot, can you see the steam in it as well as you do what comes out into the air? Now put over the tube a piece of cloth or blotting-paper which has been dipped into cold water. Does more or less steam than before come out of the tube? What is the reason for the change? Catch in a dish the liquid which flows from the mouth of the tube. Such a dish is called a receiver. Has this liquid the same taste as that in the flask? Is it just the same liquid? How does the taste compare with that of the melted ice?

This is not a good way to get much distilled water, since the blotting-paper or cloth needs to be kept constantly wet, and the process is neither neat nor convenient. The great chemist, Liebig,* invented a more convenient apparatus for cooling the steam. This apparatus is usually called a Liebig's *condenser*, steam changed

* Liebig is probably most *widely* known for his Extract of Beef, though his work in that connection was small compared with the other things he did.

into water being said to be condensed. Figure 3 shows a Liebig's condenser; the tube connected with the flask in which the distillation takes place is surrounded by a jacket in which is cold water. The cold water flows in by a tube at the lower end and flows out at the top through a tube to the waste. When a distillation is taking place, the water flowing out is slightly heated, having received heat from the steam.

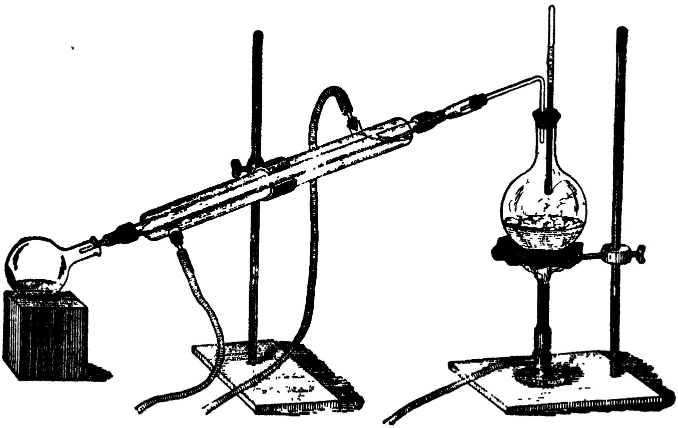


FIG. 3

EXPERIMENT 4. Partly fill a flask with water containing a little copper sulphate (the blue vitriol of commerce), put in a few pieces of broken glass or pottery, attach to the condenser, and distil. The figure represents a thermometer in the neck of the flask, which you may or may not introduce in your experiment. A liquid, when boiling in a smooth, glass vessel, is very liable to boil unevenly. For a few seconds boiling stops, and suddenly takes place with violence. It is to avoid this "bumping"

that the glass or pottery is put in. Bubbles of steam easily escape from the rough surfaces, and the boiling is continuous. What is the colour of the liquid in the flask? What is the colour of the liquid which distils? You may taste very cautiously a little of the liquid in the flask, and compare it with the taste of the distillate (the distillate is the liquid which has been distilled, and which you have caught in the receiver). How does the taste of the distillate from

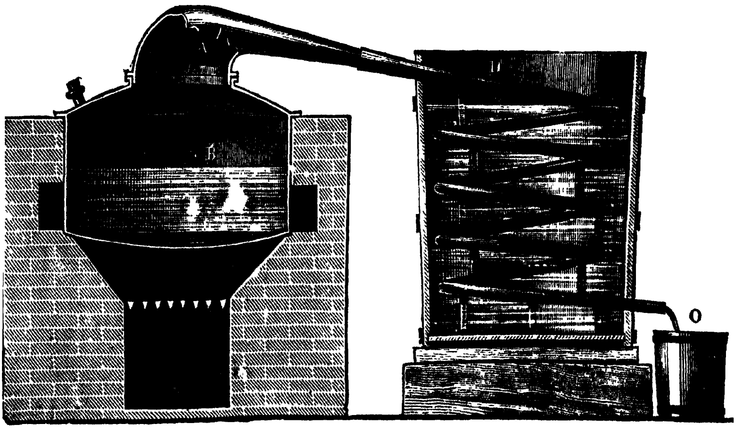


FIG. 4

the copper sulphate compare with the taste of the distillate from the salt water?

You now know the taste of distilled water. It is often said to be tasteless, or to have an insipid taste. Is it as palatable as ordinary drinking water? Figure 4 represents distillation as carried on on the large scale in the arts.

Rain-water is a product of nature's distillation on a very large scale. It is obtained from the evaporation of rivers

and lakes and seas; the vapour is cooled in the air and changed to the liquid form. Rain-water usually contains impurities taken from the air, but the purest water in nature is that which is obtained from rain or snow collected toward the end of a long-continued downfall at a distance from cities. Why is the water collected at the beginning of a heavy rain not so pure as that collected near the end? Why is the rain-water caught far out in the country purer than that in cities? What impurity would probably be contained in water caught in a clean dish on the deck of a ship at sea?

Ordinary water differs from distilled water because ordinary water has taken something out of the air or out of the ground. Rain-water contains less of other things than well-water or sea-water.

Solution in Water. — EXPERIMENT 5. Put some sugar or salt into water. What happens to the solid? Is the appearance of the water changed? Is its taste altered? The sugar or salt is said to be *dissolved*, and the liquid is called a *solution* of sugar or salt. Put some salt water into a porcelain evaporating dish or crucible; place it on the wire gauze, and heat. Let the water boil off. When most of the water is boiled away, heat carefully, moving the flame about so that the dish may not be cracked. What is left behind after the water has been evaporated? How could you tell whether distilled water is more or less pure than sea-water? Allow equal small quantities of sea-water and of well-water to stand in two dishes side by side in a warm place till they are dried up. Which leaves the greater amount of residue?

Latent Heat. — We have seen that water may exist in three forms, as solid, as liquid, and as vapour. When

the solid is heated or the vapour cooled, liquid water is obtained.

EXPERIMENT 6. Half fill with water a beaker (a glass dish something like a tumbler, but thin so that it can be heated), and heat until the water is nearly boiling. Remove the flame, put a thermometer * into the water, record the temperature, and fill up the beaker with ice, whose temperature you have already found. See whether or not all of the ice melts. Observe the temperature. Is the temperature of the water, after the ice is put in, half-way between the temperature of the hot water and that of the ice? Repeat the experiment, using *ice-water* instead of *ice*. Is the temperature after putting ice-water into the hot water higher or lower than after putting ice into the water? What does your experiment show about the heat required to melt ice?

EXPERIMENT 7. Boil water in a flask and lead the steam through a tube dipping into water which half fills a beaker, having noted the temperature of the steam and of the water. Continue the operation till the water in the beaker begins to boil. Is the beaker now full of water? Is the weight of the steam which heats the water as great as the weight of the water that has been heated by the steam? How do you explain the results that you have obtained? What do you now know about the heat required to change a solid to a liquid or a liquid to a gas? It is usual to call the heat required to convert one gramme of ice at 0° C. into water at 0° C. the latent heat of liquefaction of ice, and the heat required to convert one gramme of water at 100° C. into steam at 100° C. the latent heat of vaporisation of water. The term "latent"

* See Appendix on thermometer.

means *hidden.* The heat does not show itself by causing rise of temperature.

NOTE.— If thought best this experiment may be made more strictly quantitative. The steam that enters the water must be "dry," that is, there must be no liquid water carried over with the water vapour. Any water that condenses in the tube leading from the flask should be caught and not allowed to enter the water in the beaker. The form of trap shown at *AB* in the figure (Fig. 5) is a simple one.

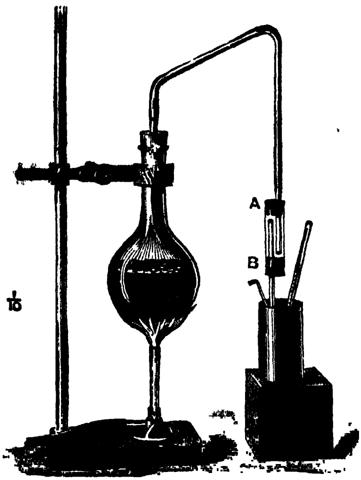


FIG. 5

Electrolysis of Water. — Having learned that ordinary water is not one simple substance, but consists of pure water with something else in it, it is natural to ask whether pure water is itself a simple substance or can be broken up, that is, separated into two or more other substances. If it is a simple substance, it will be impossible to obtain anything from it but water, just as from gold nothing but gold can be extracted. It might be possible to add something else *to* it, but not to take anything else *from* it. If we can break it up, we show that it is a compound or a mixture.

EXPERIMENT 8. Put into a dish some water made slightly acid with sulphuric acid. Fill two glass tubes *A* and *B* with this water and invert in the dish. Bend a strip of platinum so that it can be inserted in the tube *A*

as in Fig. 6 and join the platinum strip *outside the water* with a copper wire attached to the positive pole of an electric battery. Connect the tube *B* in the same manner with the negative pole of the battery.* What do you see happen on the surface of the strips of platinum? Does the water continue to fill the tubes *A* and *B*? If not, in which tube does it run down the more rapidly? Make sure that you see with which pole of the battery the tube is connected.

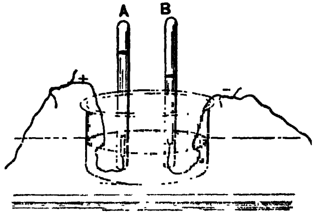


FIG. 6

Is what is in the tubes *A* and *B air?* In order to find out, remove th tubes without allowing air to enter. This may be done by putting the thumb over the mouth of the tube, if the latter is small enough; or, if not, a piece of flat glass, or a bit of cardboard. Turn the tubes mouth upward and apply a burning match to the mouth of each tube. What happens when the match is applied to the tube *A*? What happens in tube *B*? The substances in the tubes *A* and *B* that look like air are called gases. Does either of the gases act on the match as air would do? Which is least like air? The gas which was in greatest amount is called *hydrogen;* the other, *oxygen.*

* No attempt is made here to describe a current of electricity. It is assumed that the pupil understands that there is an apparatus called an electric battery; that one part of it is called the positive pole, and another the negative pole; and that if these are joined by a metal wire or other conductor a current of electricity will pass. The current may be made to pass through a liquid, provided it is a conductor and the battery is strong enough, or, to speak more precisely, has a sufficient electromotive force.

Describe the differences that you have observed between oxygen and hydrogen.

Why was sulphuric acid added to the water? In order to find out, make the experiment with distilled water, or even with ordinary drinking water. How does the action compare with the former? The things that you should see, show that the current of electricity does not pass so readily in pure water as in water containing sulphuric acid.

That the hydrogen and oxygen come from the water, however, may be shown, though you have not been able to test it, by the fact that after the operation is all over the amount of sulphuric acid in the liquid is just the same as at the beginning, and that the decrease in weight of the water is exactly equal to the combined weight of oxygen and hydrogen produced. Instead of collecting the two gases separately you may collect them in one tube; but if you do so, be extremely careful when you apply the light, for there will be a very violent explosion. If you have only a test-tube of the mixed gases there is no danger; merely turn the mouth of the tube away from you. But a larger vessel should either be surrounded by a cloth to prevent the glass from flying if the vessel should chance to break, or some other precaution should be taken to avoid possible damage. If you dry the gases (as you may do by passing them through a tube filled with calcium chloride) and collect them in a tube over mercury, and then apply a match, you should, if you look carefully, notice a thin film of moisture on the tube. This moisture is water. Is the volume of the gases greater or less than that of the water from which they were obtained, or which they combine to produce?

When hydrogen and oxygen are put together they are said to be *mixed*, or to form a *mixture;* after the light is applied they combine to form a *compound*. Is the mixture of hydrogen and oxygen or the compound formed, the more like the gases when separate? Hydrogen and oxygen have never been *decomposed*, or broken up into anything simpler, and they are therefore called *elements*.

Why were you told to join the platinum strips with the copper wire *outside* the water? In order to answer this question, try putting the two copper wires themselves into the tubes, instead of joining them to the platinum. Have you just the same appearance as before? If not, what is the difference? Smell the hydrogen which you obtain this time, unless you have done so already. A process such as that by which hydrogen and oxygen are produced by a current of electricity passing through water is called *electrolysis*. The strip of platinum at which the *oxygen* appears, and which is attached to the positive pole of the battery, is called the ***positive electrode***, or ***anode***, and the strip of platinum at which the hydrogen appears, and which is attached to the negative pole of the battery, is called the ***negative electrode***, or ***cathode***.

CHAPTER II

HYDROGEN

WE have found that water can be decomposed by a current of electricity, hydrogen and oxygen being produced. In chemistry it is very frequently the case that a compound is acted on by a substance which combines with part of it and sets the other part free. This is the principle upon which lead and other similar metals are obtained from their ores.

Decomposition of Water by Sodium and Potassium. — There are some substances that act upon water, combining with part of it, and setting free the remainder. Among these are two metals — potassium and sodium. These substances are soft and lighter than water, and as usually seen do not look like metals, being coated over with a brownish crust. They are usually kept in naphtha or some similar fluid. They can, however, be prepared in a certain way, and carefully sealed up in a glass tube containing no air, so as to present a surface quite as bright as silver. A method which shows the silvery character of the metal nearly as well as the above may be tried with sodium.

EXPERIMENT 9. Melt some paraffin wax in a *perfectly dry* test-tube. This may be done by putting the test-tube into hot water. Cut off a piece of sodium about the size of a bean, remove most of the outside crust, making it as clean as you conveniently can, and drop it into the

melted paraffin. Heat to boiling the water in which the test-tube is placed. The sodium, if pure, will probably be melted, but if not remove the test-tube from the water, dry it, and heat in the flame. Don't heat very strongly; you should merely heat enough to melt the sodium. Keep it melted for a little while till the paraffin cleans off the surface and you see a silvery white globule of melted metal. Then allow to cool. If you tip the test-tube to one side you may get the sodium to solidify against the glass and obtain a mirror. You should have about ten or twelve times as much paraffin as sodium, and never allow the latter to be uncovered.

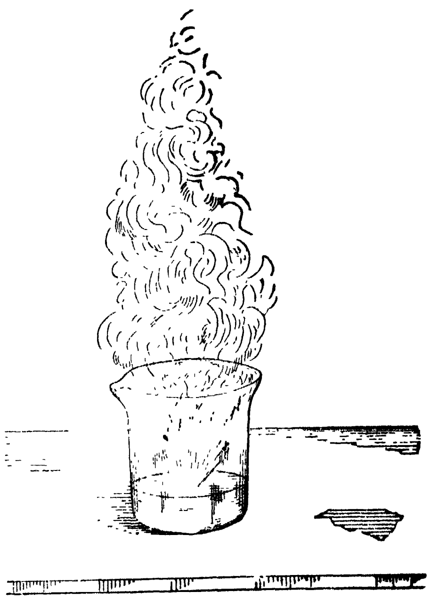


Fig. 7

Experiment 10. Throw a piece of potassium about the size of a very small pea into a dish of water. Does the potassium sink in the water or does it float? What colour has the flame? Be careful not to stand too near the dish, for the potassium may sputter, and at the end there is almost certain to be an explosion, which might be sufficient to send out a piece of the burning metal.

Repeat the experiment with sodium, being careful with it also. What shape does the sodium assume? Note how far it acts like potassium, and how far it differs. Is there a flame? Try the same experiment with *hot* water. The water should be, as in Fig. 7, about an inch deep, in a beaker not less than four inches deep. Stand off at arm's length from the beaker when you put in the sodium, and it may even be well to turn away your face. Place another piece of sodium on a bit of blotting-paper or filter-paper which is floating on the surface of *cold* water. Why is there a flame in some cases with the sodium and not in others? What is the colour of the flame? Does sodium or potassium act the more violently on water?

EXPERIMENT 11. Wrap a small piece of sodium * tightly in filter-paper in order not to enclose air with the sodium, and slip it quickly, either with the fingers or, better, with pincers, into a test-tube full of water and inverted over a dish containing water. Is there a flame this time, when the sodium is in the filter-paper? Notice the bubbles rising from the sodium. If the piece of sodium is not too large (and it should not be), these bubbles will cease before the water has all been driven out of the test-tube. Remove the test-tube carefully without allowing water to escape, and, turning it mouth upward, apply a lighted match to the gas. In what way did you get the same gas before? What is the gas?

Now examine the piece of filter-paper. Is there any

* Sodium used in this experiment must be clean, and not coated with the brown rind which forms on small pieces. Such small pieces should not be used at all, but a freshly cut fragment from the inside of a large piece, else an explosion is very liable to occur.

sodium still left? Carefully touch your tongue to the filter-paper. Also touch a piece of red litmus-paper to the filter-paper. To what colour does the red litmus change? Substances that have the taste and the action on litmus that you have noticed, are called *alkaline*. Test with litmus-paper a number of the liquids in the bottles given you, in order to see which are alkaline. Put a drop of the liquids on the paper — do not dip it into the bottles.

Pour the liquid remaining in the test-tube in which you had the sodium into a porcelain evaporating dish, and heat till the water is driven off.* Does what is left behind look like sodium? Put a drop of water on the solid, and moisten your fingers with the solution. What does it feel like? You probably noticed the same feeling when you touched the filter-paper.

We find that we get hydrogen by the action of sodium on water, and by experiments carefully carried out, it can be shown that the solid left behind when all of the water into which the sodium is put is evaporated weighs more than the sodium that is put in. It can be shown that the substance contains all of the sodium, and that it contains oxygen and some hydrogen; also that the oxygen and hydrogen combined with the sodium are not in the same proportions as in water, but that the hydrogen set free would make up the difference. In this or some similar way it can be proved that the hydrogen obtained by the action of sodium on water is derived from the water and not from the sodium. The substance with the soapy feel left

* If there is only a little water left in the test-tube, it may be necessary to add part of that in the dish. It is better to take only so much sodium as to provide enough gas to half fill the test-tube, and then, if the test-tube be removed at once, nearly all of the products of the reaction will be in it.

behind when the water was evaporated is ordinarily called caustic soda and is used for making soap.

Decomposition of Water by Iron. — A number of other metals, if heated to a sufficiently high temperature, also decompose water. The very first time that water was analysed, that is, was decomposed into its parts, was in 1783, when Lavoisier first made the experiment. His method was to heat iron filings in a tube (he used a gun-barrel) through which steam was passed. He found that the steam that went into the tube was partly used up; also, that a gas came out from the tube, and that this gas was the same as had been discovered in 1766 by Cavendish and named by him inflammable air. Lavoisier gave it the name of hydrogen (meaning water producer). Lavoisier found that the iron increased in weight, and that the weight of the hydrogen produced, added to the increase in weight of the iron, was equal to the weight of the steam decomposed. The iron was changed into a substance that Lavoisier knew to be obtained from iron and oxygen, and so he proved that water was made up of oxygen and hydrogen. When a current of electricity is passed through water, water is analysed, and both the products of analysis are obtained; but it is very seldom that an analysis is made in such a way as to give all the parts of the compound separately, nor is it necessary. Lavoisier's proof that water consists of oxygen and hydrogen was perfectly satisfactory, and it was not till several years later that water was electrolysed. It must be distinctly understood, however, that if Lavoisier had not known from former experiments that the substance into which the iron was changed was a compound of iron and oxygen, he would not have proved by the experiment

described that water is a compound of oxygen and hydrogen. Figure 8 shows a form of apparatus for repeating Lavoisier's experiment.

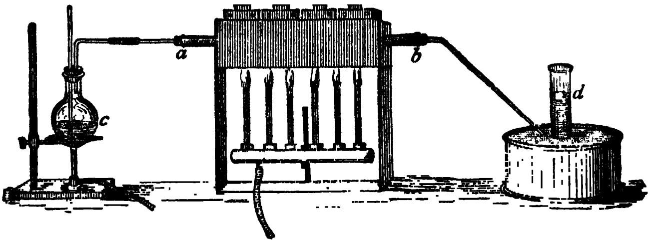


FIG. 8

Action of Sulphuric Acid on Iron and Zinc. — EXPERIMENT 12. Put into a test-tube a few iron tacks, cover them with water, and add a little sulphuric acid. Notice the smell of the gas. Apply a light to the mouth of the test-tube turned from you. (Test-tubes should always be held with the mouth turned from you, unless you are perfectly sure that nothing can happen to cause the contents to be projected from the tube. Serious accidents often happen to the eyes and face through neglect of this rule.) Does the gas seem like either hydrogen or oxygen? Does the mixture of water and sulphuric acid need as high a temperature as water alone in order to cause action on the iron?

If, when the action has ceased, there is still a considerable quantity of iron in the test-tube, pour the liquid upon a piece of filter-paper fitted into a funnel, and in a porcelain dish catch the liquid that passes through. The process that you have performed is called *filtering*, you are said to have *filtered* or to have *made* a *filtration*, and

the liquid running through the filter is called a *filtrate.* Is the filtrate more or less clear than the liquid before filtration? What is on the filter-paper? Evaporate the filtrate in the porcelain dish until nearly all of the water has been driven off, and a solid begins to appear; then allow to cool. Is there more solid in the basin when the liquid is hot or when it is cold? What does this show you about the comparative solubility of the substance in hot water and in cold? What colour is the solid? It used to be, and sometimes still is, called green vitriol, and sulphuric acid which can be obtained from it is called oil of vitriol.

EXPERIMENT 13. Use a few small pieces of zinc not specially pure, instead of the iron tacks. This time also smell the gas given off. Did the hydrogen obtained by electrolysis of water have a smell? If the smell that you noticed in any case was due to impurity, is the gas from iron or from zinc the more impure? When hydrogen is made in the laboratory it is usually made from zinc. Why?

EXPERIMENT 14. Into a beaker containing about 250 cubic centimetres (half a pint) of water, slowly pour about 25 c.c. of strong sulphuric acid. When you begin to pour, notice whether the sulphuric acid floats or sinks, or is at once lost sight of. Is the acid heavier or lighter than water? Afterwards keep stirring the solution with a glass rod, as you pour in the acid. Feel the beaker; what change of temperature do you notice? Sulphuric acid should be poured into water, and not water into sulphuric acid. Would water poured into sulphuric acid mix with it as quickly as sulphuric acid poured into water? Give a reason for your answer. Why should there be more danger of spurting when water is put into sulphuric acid than when the acid is put into water?

EXPERIMENT 15. Fit up a flask as in Fig. 9. Through one of the two holes in the cork a tube with a little funnel at the top (often called a thistle-tube, from the shape of the bulb-like funnel) passes tightly, reaching nearly to the bottom of the flask. Through the other hole a tube, bent as in the figure, passes, also tightly, a little way through the cork. Put into the flask a number of small pieces of zinc (say half a handful); pour in enough of the dilute sulphuric acid that you have prepared, to cover the zinc; fit in the cork, and see that the liquid covers the lower end of the thistle-tube. If in a minute or so gas does not come off rapidly enough, pour a very little *strong* acid down the thistle-tube and shake the flask. So soon as the gas is coming off quickly, notice whether it escapes through the thistle-tube. Put the end of the bent tube under water, and see if the gas comes out of it. Place your finger tightly over the end of the bent tube and notice the thistle-tube. Does the liquid rise in the thistle-tube? If it does not, your cork or the tubes do not fit tightly enough. Why *should* the liquid rise? What two uses does the thistle-tube serve? What would happen if there were no thistle-tube, and the other tube got stopped up when the gas was being produced rapidly? Why is the thistle-tube sometimes called a safety tube?

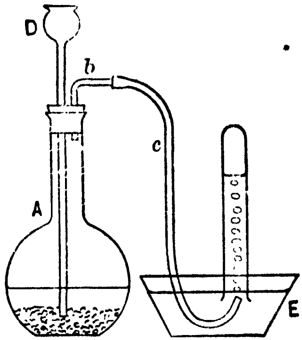


FIG. 9

Experiments with Hydrogen. — Place the end of the bent tube under water in a dish (usually called a pneumatic

trough, because used for collecting gases,—the Greek word *pneuma* meaning a gas).

Fill a small cylinder, or a test-tube, with water in the pneumatic trough, and invert it. Place the end of the tube from which the hydrogen is escaping under the mouth of the cylinder and collect the gas. When the cylinder is full, remove it and carefully apply a lighted match or taper. If there is an explosion, let the gas escape for a while longer, and try again, until the gas burns quietly. Then collect several cylinders of hydrogen.

Place one cylinder mouth upward on the table, and hold another mouth downward for a minute; then apply a lighted taper to the mouth of each cylinder. Hold a cylinder of air mouth downward, and bring beneath it a cylinder containing hydrogen, as in Fig. 10. In a minute, or somewhat less, apply a taper to the mouth of each jar. Is hydrogen lighter or heavier than air? How has your experiment given you the information?*

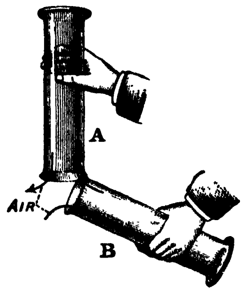


Fig. 10

Hold a cylinder of hydrogen mouth downward and push a lighted taper far up into the gas. Does the taper continue to burn? Does hydrogen *support the combustion* of the taper? Hydrogen would act with all the ordinary substances that burn as it does with the taper. Is it a *supporter of combustion?*

* As an amusement soap-bubbles may be blown. This may be done with an ordinary soap lather and a clay tobacco pipe; but Newth recommends a soap solution made in the following way: 10 grammes of sodium

Invert a cylinder over the pneumatic trough and let out air till the water runs up two-sevenths of the height. *Then place a cylinder of hydrogen with its mouth below* the first cylinder and introduce enough hydrogen to fill it. Your cylinder now contains a mixture of hydrogen and air in the proportion of 2 to 5. Remove the cylinder in the ordinary way and apply a taper to its mouth. Hydrogen and air mixed in the above proportions give a more violent explosion than when mixed in any other proportion.

Gas has doubtless now ceased to come off from the generating flask. If there is zinc still present, as there probably is, add more acid. Does hydrogen begin to come off? If so, is it proved that hydrogen comes from the acid? If you mix sulphuric acid and water, there is no hydrogen evolved; but if you add zinc, hydrogen is formed. Does that fact prove that hydrogen comes from the zinc? If you are told that zinc is an element and that after the hydrogen has been made there is just as much water in the flask as there was at the beginning of the operation, what is your conclusion as to the source of the hydrogen?

oleate and 400 c.c. of distilled water are placed in a stoppered bottle and allowed to stand, without warming, till the oleate is dissolved. 100 c.c. of pure glycerine is then added, and the mixture, after being well shaken, is allowed to stand in the dark for a few days. The clear solution is then carefully decanted into a second stoppered bottle and one drop of strong ammonia solution added. If kept in the dark and not exposed to the air, this solution may be preserved for years.

The hydrogen may be supplied by the generating flask if passed through a tube 10 centimetres long containing cotton wool, and the bubbles are best made by using a thistle-tube instead of the tobacco pipe. As soon as the bubble begins to form, turn it upward, and when it is almost ready to leave the thistle-tube bulb, give the latter a slight jerk so as to detach the bubble easily.

If the hydrogen is coming off pretty rapidly, collect a small cylinder ful' to make sure that the gas will burn quietly. Remove the delivery tube from the water and attach to it, by a piece of rubber tubing, a glass tube whose farther end is drawn out so as to form a narrow opening or jet. Clamp this tube in an almost upright position; wrap the flask in a cloth and light the gas as it escapes from the jet. What is the colour of the flame? Put a piece of fine iron wire into the flame. Is the flame more or less hot than a candle, lamp, or gas flame? Does it give more or less light? Try wire or thin shavings of other metals in the same flame. Do you now see why the tube was not placed vertically?

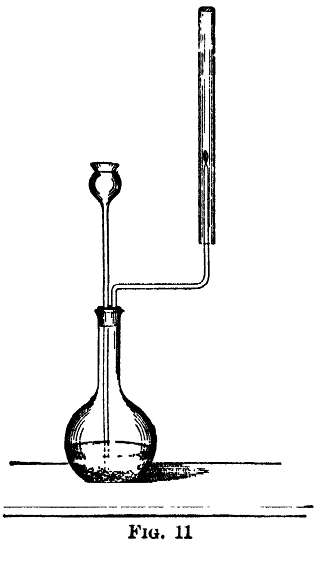


FIG. 11

For the *next* experiment place the tube vertically. Put down over the burning jet a tube open at both ends, as shown in Fig. **11**. You should get a musical note, but it may be that the tube is not the right size in proportion to the flame, in which case there will be no sound. Try tubes of different lengths and different diameters, and see how the note varies. The note produced is really the sound of a series of explosions, and the pitch of the note depends upon the rapidity with which these explosions take place; the more frequent the explosions, the higher the note.

Place over the jet a retort fitted up as shown in Fig. 12. The bent tube reaching nearly to the bottom of the retort is to serve as a draught. What do you see in the retort after the jet has been burning a little while? If the retort gets so hot that you see steam escaping into the air, through the small tube, cool the retort by putting over it a piece of cloth dipped into cold water. After half an hour or so you will probably have enough liquid to experiment with.* What does it taste like? Pour the liquid into a test-tube and put in a thermometer. Then place the test-tube in a mixture of snow or ice and salt. So soon as the liquid in the test-tube begins to freeze, look at the thermometer. Stir the liquid with the thermometer to make sure that it is the same temperature throughout. What is the temperature? Take out the thermometer and keep the test-tube and liquid. Now put the thermometer into another test-tube containing distilled water, and freeze the water. What is its temperature of freezing?

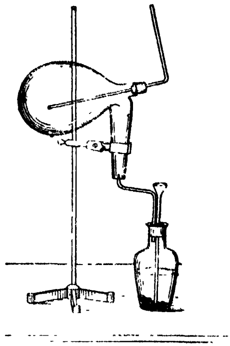


FIG 12

Heat the liquid in the first test-tube until it boils and hold the thermometer in the vapour. What is its temperature? Do the same with distilled water. What is its temperature? What do you conclude the liquid to be,

* It may be convenient for all the members of the class to pour the liquid obtained into one test-tube so that there will be sufficient for the tests. If it is thought advisable, the gas may be dried before burning it, though that seems an unnecessary refinement.

which you got by burning hydrogen in air? What must the air contain, since hydrogen burning in it gives this liquid?

EXPERIMENT 16. Grind up some red hematite and see whether it is attracted by a magnet. Put it into a glass tube, open at each end. Through a cork at one end pass a tube which is connected with a hydrogen apparatus. To the other end of the tube containing the hematite attach a bulb tube or some sort of apparatus for collecting the vapours produced by the reaction. The figure (Fig. 13) represents a suitable arrangement. After air has been driven out of the apparatus, heat the tube containing hematite. What do you see coming out from the tube? Decide whether or not the liquid which condenses in the bulb tube is water. Allow the tube with the hematite to cool. What colour has the powder now? Is it attracted by the magnet? What two things are there in red hematite? Is red hematite a mixture or a compound of these two substances?

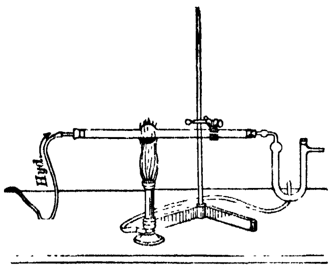


FIG. 13

The composition of water may be determined either by analysis — that is, breaking it up into its components — or by synthesis — that is, producing it by the union of these components. In what experiments did you analyse water, and in what experiments did you synthesise it?

Now filter the liquid in the flask, evaporate the filtrate in a porcelain dish until a solid begins to form, and allow

to cool. What is the colour and shape of the solid crystals? These crystals contain the zinc that was dissolved, along with a part of the sulphuric acid used. Sulphuric acid was divided into two parts — hydrogen, which appeared as a gas, and another part which united with the zinc to form *white vitriol*, or, as the chemist usually calls it, zinc sulphate.

If you had weighed the zinc and weighed the strong sulphuric acid (not the dilute acid), you would have found that a little more than 60 grammes of zinc were dissolved by 100 grammes of acid. Why was the sulphuric acid *diluted* (mixed with water) before being put upon the zinc? In order to find out, put some zinc into a test-tube and pour in a little strong sulphuric acid. Does strong acid act more or less rapidly than dilute?

Statement regarding the Occurrence, Preparation, and Properties of Hydrogen. — As it is impossible for us to create anything, any substance that we work with must either be found ready made in nature, or must be made from something else that is found in nature. Only a few of the elements are found ready made; most of them have to be separated from compounds. Books of chemistry very frequently describe an element under three heads — its occurrence in nature, its preparation, and its properties. You should never be satisfied when you are studying a chemical substance until you have pretty clear ideas on these three points. Since hydrogen burns in air you would naturally not expect to find any large quantity in the atmosphere. As some of the hydrogen that you made escaped into the air without you *seeing* it burn, it is just possible that a little might exist in the air unburned, and lately an investigator claims to have found one

part of hydrogen by volume, in about 100,000 parts of air.

You have found that hydrogen exists in water. One-ninth of the weight of water is composed of hydrogen, which also exists in all vegetable and animal tissues.

You know several ways in which hydrogen is prepared; what are they?

You have found out many of the properties of hydrogen. The properties of a substance are usually divided into *physical* and *chemical*. Suppose we take the physical properties first.

What is the physical state of hydrogen, solid, liquid, or gaseous? What is its colour? smell? taste? What is its density? To all of these questions you can give at least partial answers.

Though hydrogen is a gas at ordinary temperatures, it would become liquid if made cold enough. There is such difficulty, however, in lowering the temperature sufficiently that it was not liquefied, at all events in any appreciable quantity, till 1898. Liquid hydrogen boils at $-252.5°$ C. and freezes at $-256°$ C. Hydrogen is very sparingly soluble in water. At 0° C. 100 volumes of water can dissolve 2 volumes of hydrogen. Usually gases that are difficult to condense are sparingly soluble.

The gas hydrogen is the lightest substance known, being less than one-fourteenth as heavy as air. It has been used for balloons on that account, but coal-gas is more suitable, being cheaper and not so liable to leak from the balloon.

Pure hydrogen is colourless, odourless, and tasteless. It is not poisonous when perfectly pure, but hydrogen from zinc may contain a little arsenic, because the zinc, unless specially purified, is liable to contain arsenic, while hydro-

gen from iron has very disagreeable impurities. Though hydrogen is not poisonous, one cannot live in an atmosphere of hydrogen any more than in water, for oxygen is necessary to support life. Let us now consider the chemical properties of hydrogen. You have seen the principal one, namely, its great affinity for oxygen, with which it combines, producing great heat, always a sign of vigorous action. More heat is produced by the union of hydrogen and oxygen than by the same weight of any other two substances. The heat produced by the union of 2 grammes of hydrogen with 16 grammes of oxygen in the formation of 18 grammes of water is sufficient to heat from 0° C. to 1° C. about 68,400 grammes of water, or nearly four thousand times its own weight.

To change ice into water requires considerable heat; to change water into steam requires a greater amount of heat; to change steam into the gases hydrogen and oxygen requires a still greater amount of heat.

It requires exactly the same amount of heat to decompose water into its constituents as is produced by their combination. When water is decomposed by a current of electricity heat is practically used up, for the same current might have been employed in heating an electric stove.

CHAPTER III

OXYGEN

WE have seen that when water is electrolysed oxygen as well as hydrogen is produced, and a good deal of oxygen is now made in this way; but in laboratories not supplied with electrical power other methods are used.

We saw that hydrogen can be obtained from water by the action of substances which take away oxygen, and it might be possible to produce oxygen from water by the action of something which would take away the hydrogen. There is no *convenient* substance for doing this, however.

If steam is heated to a sufficiently high temperature it is decomposed into oxygen and hydrogen, but it is not *easy* to separate the two gases, though it is not impossible to do so.

We found that oxygen exists in the air, but in this case also it is difficult to separate the other constituents which are with it in the atmosphere.

Oxygen obtained from Compounds by Heat. — There are some substances containing oxygen which decompose on being heated, yielding oxygen gas. In 1772 the Swedish chemist Scheele obtained it by heating nitre, a substance which is often called saltpetre, and which chemists now call potassium nitrate. Scheele named the gas "fire air," because of the great readiness with which many substances burn in it. The name oxygen was not given till some time afterward.

In 1774 an Englishman, Priestley, not knowing of Scheele's work, discovered the gas by heating red lead, a *substance used in the manufacture of some red paints.* Priestley later on used "red precipitate" or "calcined mercury" as a source from which to obtain the gas.

EXPERIMENT 17. In a small dry test-tube heat a little calcined mercury (called now mercuric oxide). To what colour does the mercuric oxide change when first heated? After a minute or two examine the upper part of the tube. What do you see? Put into the mouth of the test-tube a glowing match, or pine splinter. What happens? With a splinter of wood or an iron wire gather together into a globule the substance in the upper part of the test-tube. What is the substance? What two substances are in calcined mercury. You now see why the name mercuric oxide is given to the substance. What two substances are in black oxide of manganese. Black oxide of manganese is a solid which, if heated strongly enough, will also give oxygen, red oxide of manganese being left behind. Does the black or the red oxide of manganese contain the more oxygen? The black oxide of manganese needs to be heated more strongly than mercuric oxide, in order to yield oxygen.

EXPERIMENT 18. Heat in a test-tube a little potassium chlorate (called by druggists chlorate of potash and sold in the form of crystals or as tablets for sore throat). After the solid is melted, watch carefully to see whether gas comes off immediately or whether the substance needs to be heated more strongly. After the gas has come off for a little time, test it with a glowing match. What is the gas? Now drop a little powdered black oxide of manganese into the test-tube, taking care, *as always*, that

the mouth of the tube is turned from you. Do you see any difference? If so, what?

Experiments with Oxygen. — EXPERIMENT 19. Mix about 20 grammes of potassium chlorate, which you weigh roughly, with about one-quarter its weight of black oxide of manganese (manganese *dioxide*). Put the mixture into a small retort or large test-tube and fit up in such a way

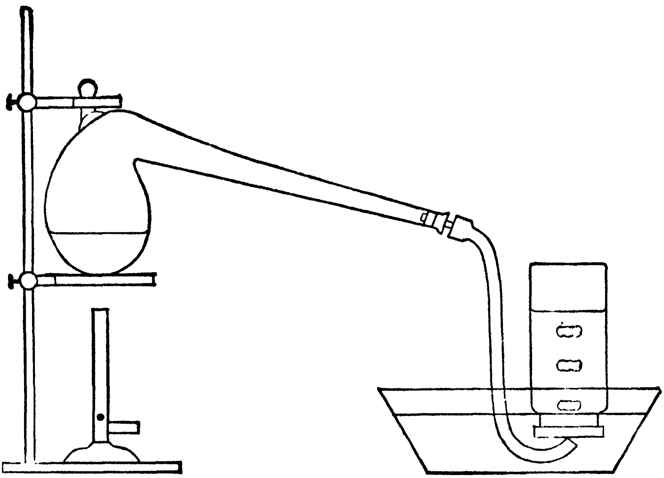


FIG. 14

that you can collect over water the gas which is produced when you heat the mixture. Figure 14 shows a retort and a method which may be employed. Collect a number of cylinders of the gas. When you have finished collecting the oxygen, take the delivery tube out of the water or open the retort or test-tube in some way. Why do you do this? Does a gas occupy more volume when hot or when cold?

Into one cylinder * pour a little lime-water and shake it up in the cylinder. Does the oxygen apparently make any change in the lime-water? Now heat a piece of charcoal till it glows and introduce it into the cylinder, keeping the mouth of the cylinder covered as much as possible. Does the charcoal glow more or less brightly? Does it produce a flame? After the charcoal has been in a minute or two, take it out and shake up the lime-water once more. What change do you notice in the lime-water?

Light a candle and when it is burning properly, notice the size of the flame. Blow it out and while the wick is still red, introduce it into a cylinder of oxygen. What happens? Is the flame of the candle burning in oxygen larger or smaller than that of the candle burning in air? Is it more or less bright? Cover the cylinder while the candle is burning, so that no air can enter. What change do you notice after a while in the flame of the candle? When the candle goes out, remove it from the cylinder and introduce some lime-water. How is the lime-water affected? Have you any reason for suspecting that there is the same substance in the candle that there was in the charcoal? Has your experiment given you a *complete* proof? Did the fact that potassium and sodium decomposed water prove these two substances identical?

Heat some sulphur in a deflagrating spoon (a deflagrating spoon is like a small ladle and is called a *deflagrating*

* The glass jars used for preserving fruit are very good vessels for containing gases, as they may be closed air tight. In cases in the text where cylinders are spoken of for collecting and preserving gases, these vessels may be employed with advantage, provided small enough ones can be obtained. Common wide-mouthed bottles holding two or three ounces or from seventy-five to one hundred cubic centimetres may be used in most cases.

spoon because ordinarily employed to hold substances that are to be burned). When the sulphur begins to burn, notice the smell of the fumes and then introduce the burning sulphur into a cylinder of oxygen. How does the flame compare with that in the air? When the sulphur ceases to burn, put a little water into the cylinder, and shake. Is the smell of the gas in the cylinder or of the solution in water similar to, or different from, what was obtained in air? Matches often have sulphur on them, and the smell of sulphur burning in air is often called the smell of burning matches. Moisten a piece of blue litmus-paper with some of the solution in the cylinder. To what colour does the paper turn?

In another cylinder of oxygen perform a similar experiment with phosphorus. Phosphorus is very easily set on fire, so must be handled very carefully. Cut off under water a small piece of phosphorus, say half the size of a pea or less. Why is phosphorus kept under water, and why must it be under water when it is cut? * Are potassium and sodium kept under water to protect them from the air? Dry the small piece of phosphorus on blotting-paper or filter-paper by laying it on the paper, which is then folded over it without *rubbing* the phosphorus. Why should the phosphorus be dried? Why should it be dried on *bibulous* paper, such as blotting-paper or filter-paper? Put the phosphorus into a deflagrating spoon and heat gently until it begins to burn, and then plunge

* Phosphorus inflames so readily and burning phosphorus inflicts such severe wounds that beginners are often warned not to take it in their fingers except when it is under water, but to hold it in nippers. When held in nippers, however, the phosphorus is liable to be more carelessly handled, and, therefore, more frequently to catch fire inopportunely. In whatever way phosphorus is handled, the greatest care must be exercised.

into a cylinder of oxygen. What does the smoke look like? As soon as the phosphorus has ceased burning, remove it from the cylinder, pour in a little water, and shake. What happens to the fumes? Taste a drop of the water. What taste has it? How does it act on blue litmus-paper? Substances that have a sour taste and that redden blue litmus are called acids. Test with litmus the liquids in the bottles given you, to find out which are acid, which alkaline, and which neutral, that is, neither acid nor alkaline. Add lime-water to some of the water in the cylinder and compare with the result obtained after burning carbon. Lavoisier, the celebrated French chemist, who, though he did not discover oxygen, was the most thorough investigator of its character, thought that all acids contained it, and so gave to the gas the name oxygen, which means acid producer. It was later found that all acids do not contain oxygen, but the name was retained. The name hydrogen, as already stated, is also due to Lavoisier.

Set fire to a piece of sodium in a deflagrating spoon and introduce it into another cylinder of oxygen. What is the colour of the flame, and what appearance have the fumes? Pour a little water into the cylinder and test the solution with litmus. Is it acid, or alkaline, or neutral?

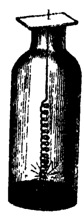


FIG. 15

Heat a watch-spring in a flame and straighten it, leaving a little of the spiral at one end, or use instead a piece of picture-cord wire. Dip the end into sulphur, light it, and introduce the wire into a cylinder of oxygen having water about an inch deep in the bottom, as shown in Fig. 15. Notice how the iron burns. Does it give off fumes like sulphur, phos-

phorus, and sodium? Does it have a flame? What happens to the product of combustion? Why were you told to have water in the bottom of the cylinder? Take out the pieces of solid, wash them off, and test them with litmus-paper. Is the litmus affected? Can you give any reason why you might have expected the result obtained? Is the solid soluble in water? What was the reason for washing it off before testing it with litmus? What is in solution in the water in the cylinder? Does this compound of iron and oxygen look like red hematite, which you have already proved to be a compound of iron and oxygen? What difference, if any, is there in the action of each of these oxides toward a magnet? What properties have you noticed of the oxides examined, of carbon, sulphur, phosphorus, sodium, and iron?

Residue after Preparation of Oxygen. — If you have not already made sure that all of the oxygen has been given off from the mixture, heat it once more till no more gas is evolved. When the residue is cool, add enough water to dissolve out all except the black substance, and filter. Is what remains on the filter like, or is it not like, one of the substances put into the mixture? What is it? Evaporate the filtrate to dryness. What part of the original mixture does it most resemble? Is it exactly the same? Does it weigh more or less? Find out approximately how the weights compare. Compare also the taste of the substance with that of potassium chlorate. Take equal amounts of the two substances in separate test-tubes, and add just enough water to dissolve each of them in the cold. Which is the more soluble?

Statement regarding the Occurrence and Properties of Oxygen. — Oxygen is not only found in water and in air,

but it forms about one-half of the solid crust of the earth, so that it is the most abundant substance in nature. It forms part of every vegetable and animal tissue. It is not easy to separate it from the great majority of its compounds, and so comparatively expensive substances are used for its manufacture.

It is a colourless, odourless, tasteless gas at the ordinary temperature. It was first liquefied in very small quantities in 1877; it can now be obtained liquid by the gallon. It boils at $-182.5°$ C. It is just a little more soluble in water than hydrogen is, 100 volumes of water taking up about 3 volumes of oxygen at the ordinary temperature.* The solubility of oxygen in water is very important, for it is the dissolved oxygen that enables fish to live. If water boiled, to drive out the oxygen, and then cooled in absence of air, fish cannot live in it.

Oxygen is the part of the air that supports life, but if the air were all oxygen the actions of life would go on too rapidly. In some cases, however, it is used in hospitals for patients in whom respiration needs to be stimulated. Oxygen is slightly heavier than air and sixteen times as heavy as hydrogen.

Oxygen is necessary not only for life but for the combustion of all ordinary fuels. Its most striking chemical property is the number of substances with which it can combine, and the very firm compounds which it makes with many of them.

* Gases are more soluble at lower temperature than at higher, and hence, when the solubility is given, the temperature should be indicated. Hydrogen between the temperatures 0° C. and 25° C. was said to be an exception, the solubility being the same at all temperatures within that limit, but later investigations show that it follows the general rule.

You have learned that when it combines with an element, the compound is called an oxide, and sometimes it combines with an element in several proportions, — that is, there are several oxides of the one element. These oxides have different characters, sometimes very different indeed. The properties of a substance depend not only on the elements which compose it, but also upon the proportions of the element. This you saw illustrated in the case of hematite and the other oxide of iron which has the same composition as the mineral magnetite.

Ozone. — When electric sparks are passed through oxygen, a small quantity of the gas is changed and acquires a very strong smell. The new substance is called *ozone*, from a Greek word which means a smell. Though ozone is made from oxygen, this fact does not prove that oxygen is not a simple substance, for there is no loss in weight, and on being heated to a temperature of 300° C. the ozone is reconverted into oxygen. The same simple substance can appear in two forms, one of which is called oxygen, the other ozone. They are said to be allotropic forms (from the Greek word meaning "another form"), or, since oxygen is the more common, ozone is often said to be an allotropic form of oxygen.

The properties of ozone and oxygen are very different in many respects. Ozone is one and one-half times as heavy as oxygen. It acts more readily on most substances than oxygen does; for instance, silver, which is not acted on by oxygen, is acted on by ozone, forming silver oxide. It also acts on potassium iodide, setting free iodine, which gives a blue colour to starch. A usual test for ozone is a piece of filter-paper moistened with a solution of potassium iodide and starch. If ozone is present the paper

turns blue. Such papers are often used to test the presence of ozone in the atmosphere. Some other gases also give the blue colour to starch paper, and unless they are known to be absent the test is not sufficient. Many coloured substances become colourless if oxygen is added to them. Ozone is a form of the element which acts on these colours more readily than ordinary oxygen does, and takes away the colour, or, as we usually say, *bleaches*. Hence ozone is sometimes used as a *bleaching agent*, though some other bleaching agents are more important. Ozone is also sometimes employed in the *refining* of oils and for other industrial purposes. It will probably come into extensive use, now that electrical power is so widely employed. Ozone can be made in other ways, but none of them are so cheap or so satisfactory. Ozone destroys the disagreeable odour of many substances, and is therefore used as a *disinfectant*.

Not only is ozone produced by ordinary electric machines, but it is made on the large scale by electric discharges in the atmosphere. This is one reason why, after a thunderstorm, the air seems so pure and fresh. There is less ozone in cities than in the country, because it is more quickly used up in cities. The air over the ocean contains a comparatively large amount of ozone, and there is very good reason to think that the action of ozone has a great deal to do with the phosphorescence so frequently seen at sea.

Ozone can be condensed to a liquid, in which condition it is of an indigo blue colour. The liquid boils at $-119°$ C., and the vapour has a slightly blue tinge. It has been suggested that the colour of the sky is caused by ozone.

Hydrogen Peroxide. — Water is an oxide of hydrogen, but there is another oxide which contains more oxygen in proportion to the hydrogen and is called hydrogen peroxide. The prefix "per" is a contraction for "hyper," as in the word hypercritical. The term "peroxide" denotes that there is a large amount of oxygen in the substance. In hydrogen peroxide there is twice as much oxygen in proportion as in water, and it is sometimes called hydrogen dioxide to show this fact. In hydrogen peroxide the hydrogen and oxygen are not so firmly united as in water. We might expect that this would be the case, because if it were not, hydrogen peroxide would probably be as common as water. Since hydrogen peroxide is not so firm a compound as water, in other words is not so stable, it might be expected to give up part of its oxygen to other substances. This it does, acting as an oxidising agent and being itself *reduced* to water. Hydrogen peroxide is therefore used in bleaching, being sometimes more convenient for that purpose than ozone. It is also a disinfectant and is used in surgery.

Like water, hydrogen peroxide is a liquid, but it is heavier than water. It readily decomposes into water and oxygen, and is used in dilute solution because more stable in that condition. The ordinary commercial solution in water contains about 3% of the peroxide, but lately with very special manipulation and precaution a liquid has been obtained that contains 99% of hydrogen peroxide.

CHAPTER IV

NITROGEN

WE have found that the air contains oxygen, but that it is not pure oxygen, because substances do not burn in it so readily as in the pure oxygen that we prepared. Which substance burned most readily in oxygen? Which substance required the most care in handling Phosphorus is the best substance for rapidly taking away oxygen from the air.

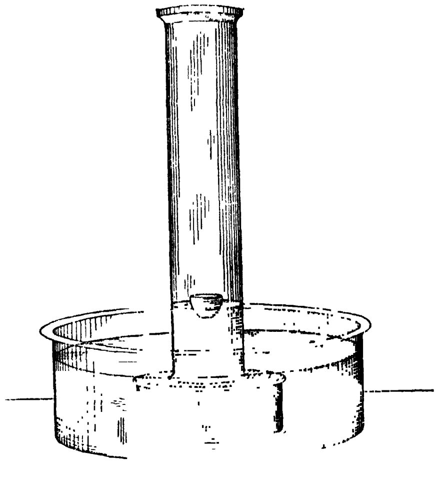


FIG. 16

Action of Phosphorus on Air. — EXPERIMENT 20. Just as carefully as before, cut off a piece or two of phosphorus (about half the size of an apple seed), dry and put into a small porcelain dish floating in a pneumatic trough. Set fire to the phosphorus and immediately place over it an inverted cylinder as in Fig. 16. Do bubbles escape from the cylinder? If so, why? If not, what prevents

them escaping in *your* experiment? Does the flame of the phosphorus grow more or less bright? Does it grow larger or smaller? Why? What is the appearance of the fumes in the cylinder? Allow to stand for a few minutes. What becomes of the fumes? Put a piece of litmus-paper into the cylinder and see what colour it assumes. Notice the height of the water in the cylinder. Why has the water risen? Remove the cylinder from the pneumatic trough and test the gas with a lighted match or taper. Does the match continue to burn? Does the gas take fire? Is the gas a supporter of combustion? Is it combustible?

EXPERIMENT 21. Invert a graduated cylinder over the pneumatic trough. Allow air to escape till there is 100 c.c. or 200 c.c. (as may be most convenient) in the cylinder, the water being at the same level inside and outside. Take the reading carefully. Then introduce a piece of phosphorus as large as a bean or larger, supported on a wire so that it will be above the surface of the water (Fig. 17 shows the apparatus, a stick of phosphorus being represented). After a day or two remove the phos-

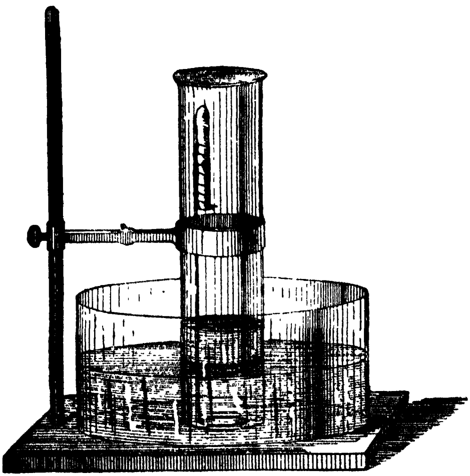


FIG. 17

phorus and again measure carefully the volume of the gas, the level of the water inside and outside being, as before, the same. Assuming that the oxygen has all been removed by the phosphorus, what does your experiment show you as to its proportion by volume in the air?

Copper heated in Current of Air. — EXPERIMENT 22. Fit up an apparatus as in the figure (Fig. 18). In the bulb of the glass tube, as shown at the left of the figure, place

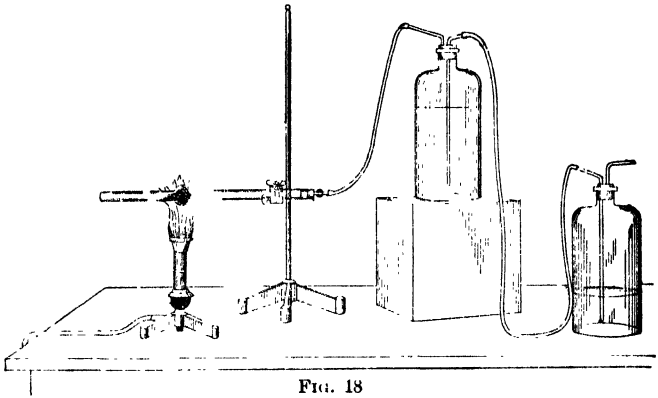


FIG. 18

fine copper filings. Put the tube into position and apply heat. When the copper is red hot, pass air *slowly* over it, allowing time for the copper to act on the air.* One of the easiest ways to provide the current of air is by means of an aspirator. A form of aspirator that may be used is shown in the figure. A bottle filled with water is fitted

* Unless the copper is porous it may become so coated with oxide as to be ineffectual. This is avoided by passing the air through ammonia water. If this is done, however, the appearance of the copper will not be much changed, the oxide not being produced, and the further experiment of passing hydrogen over the oxide cannot be performed.

with a cork having two holes, through one of which a tube passes to the bottom of the bottle. This tube has attached to it a rubber tube long enough to act as a siphon and closed by a pinch-cock or screw-clamp. A short tube passes just through the other hole in the cork and is connected with the larger tube containing the copper. As the water is allowed to flow out of the bottle air is drawn in, and its flow may be regulated by the pinch-cock. The figure represents the water as flowing into a second bottle. The pinch-cock on the tube between the bottles is omitted in this diagram but is shown in the next. The current of air is from left to right. When you have collected a sufficient quantity of the gas, transfer some of it to a cylinder or test-tube. Figure 19 shows one method of doing this; the bottle containing the gas being now placed on the table and the other one on the block.

Experiments with Nitrogen. — Find out whether the gas has any smell, taste, or colour, and try its effect on a burning match. Add to another test-tube or cylinder full of the gas, a little lime-water or baryta-water. Is there or is there not any change in the solution? This experiment is for the purpose of comparison at a later date. The gas that you have prepared is nitrogen. What is the appearance of the substance in the glass bulb? Is it copper? Without removing it, pass hydrogen over it and heat. What passes out from the bulbed tube? What does the hydrogen remove from the black substance in the tube? What name would you give to this black substance?

Nitrogen is slightly lighter than air. It is less soluble in water than oxygen is; 100 volumes of water dissolve $1\frac{1}{2}$ volumes of nitrogen at the ordinary temperature. Nitrogen can be condensed to a liquid, which boils at $-195°$ C

Argon. — We have found that nitrogen exists in the air. It is found in many other substances, among them many tissues of plants and animals, though not existing in all the tissues as oxygen and hydrogen do.

From these substances the nitrogen can be obtained, and a few years ago it was discovered by Lord Rayleigh that nitrogen so obtained is very slightly less dense than nitrogen obtained from air. This led him to conjecture

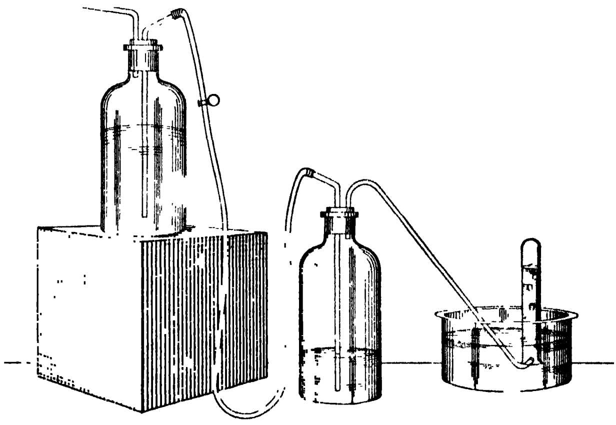


FIG. 19

that the nitrogen obtained from air is not pure, and Professor Ramsay and Rayleigh succeeded in separating from the nitrogen of the air a substance which is not known to combine with anything else, and to which the name *argon*, meaning inert, was given. Further experiment indicated that what was first called argon contains small quantities of other inert gases. Why is there no argon in the nitrogen which is obtained from compounds?

Composition of Air. — Air consists mainly of oxygen and nitrogen. The proportions of oxygen and nitrogen in air are not *exactly* the same at all times in any one place, nor are they exactly the same in all places at any one time, but the variations are within very narrow limits. When Scheele discovered nitrogen in 1772 he called it "vitiated air," because he found that when the "fire air" was removed from ordinary atmospheric air, what was left behind could not support life. Hence, when later on experiments were made to find out the proportions of oxygen and nitrogen in air, the apparatus used was called a *eudiometer*, which means measurer of goodness.

The variations in the amounts of oxygen and nitrogen in the air are not large enough to make any difference in its wholesomeness, but the name has been retained for this apparatus, which is very much used in the analysis of gases. One form consists of a straight graduated tube closed at one end, and provided with two platinum wires going through the glass so that an electric spark can be passed between them through the gas in the tube.

In order to find out the proportions of oxygen and nitrogen (along with argon, etc.) in the air, the eudiometer is filled with mercury, inverted over a mercury trough, and partially filled with air which has been freed from all other gases. Sufficient hydrogen is then passed in, the mixture is fired by an electric spark, which causes the oxygen and hydrogen to unite forming water whose volume is very small, and the volume of both oxygen and nitrogen can thus be determined. Another form of apparatus is shown in Fig. 20. There are a great many details and precautions not mentioned in this description.

In the case of oxygen and hydrogen, you saw the dif-

ference between a mixture and a compound. Would you consider that air is a mixture of oxygen and nitrogen or a compound?

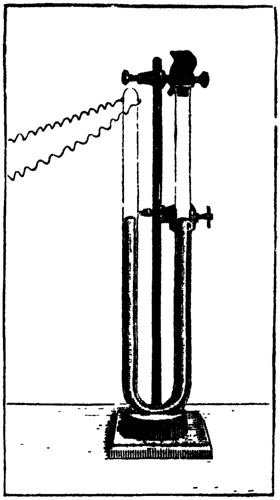


FIG. 20

Liquid Air.—Air was liquefied for the first time in 1877, when a few small drops were obtained. Now it is manufactured by the gallon. Liquid air has many very peculiar and interesting properties, but among the most interesting are the effects produced by its extremely low temperature. If liquid air is put into a tin cup and allowed to stand till the cup gets quite cold, the latter becomes very brittle, and may be broken in the hand more easily than an ordinary glass dish of the same thickness would be at the ordinary temperature. Mercury freezes in liquid air, and a nail may be driven by a hammer made of the frozen metal. Bread becomes crisp, like very dry toast, and crumbles between the fingers. Alcohol freezes to an ice which looks something like the white frosting of a cake.

Perhaps one of the most striking experiments is boiling liquid air in a tea-kettle over a gas-burner. The air in boiling keeps the kettle so cold that hoar frost collects on it. The moisture that condenses on the kettle comes chiefly from the gas flame. What does this show one of the constituents of gas to be? If the kettle of liquid air is taken from the fire and a cupful of water poured into

it, the air boils more rapidly than when heated by the gas-burner, because the water mixes with the air and heats it throughout. The kettle may be now put on the fire again, and ice produced by the freezing of the water taken out of it.

Both oxygen and nitrogen boil at very low temperatures, but nitrogen boils at a lower temperature than oxygen, and so in the liquid air nitrogen can be boiled off from the oxygen, just as alcohol can be boiled off from water. It may be that, sometime, the cheapest way of getting oxygen will be to liquefy air and boil off the nitrogen.

Liquid oxygen is somewhat magnetic, and if a strong electromagnet be brought down over liquid oxygen, the latter rises up toward the magnet. This is a very interesting property.

AMMONIA

Destructive Distillation. — EXPERIMENT 23. Heat a small quantity of horn or lean meat or hair in a test-tube. Notice what collects in the upper part of the tube. What evidence is there that the substance used contains oxygen and hydrogen? If, when you distil water from a salt solution in a flask, you pour back the distillate into the flask, would the liquid produced be the same as at first, or would it be different? If the substances that distil from the horn or meat or hair were brought back into the test-tube, would the original substance be reproduced? When by heating a substance the products of distillation cannot recombine to produce the original substance, there is said to be *destructive* distillation. When meat is heated, is there *simple distillation* or *destructive distillation?*

Into the vapours coming off from the test-tube put a strip of moistened neutral litmus-paper. To what colour does the litmus change? What does this show? The substance producing this effect is called ammonia, but in this case it is mixed with a number of other substances.

Laboratory Preparation of Ammonia and Experiments with the Gas. — EXPERIMENT 24. Test a crystal of sal-ammoniac (ammonium chloride) with moistened litmus-paper to find out whether it is alkaline, neutral, or acid. Do the same with a little lime. Mix a few grammes of ammonium chloride with about twice its weight of lime, and introduce into a small retort or large test-tube. Fit up the apparatus so that you can collect any gas coming off from it, and heat. Hold a piece of moistened litmus-paper at the mouth of the delivery-tube. What evidence have you that a gas is being produced in your apparatus? Collect the gas, not over water, but as shown in Fig. 21, in a test-tube (or small cylinder) by inverting the test-tube and putting the delivery-tube of your apparatus far up into the test-tube, whose mouth is loosely

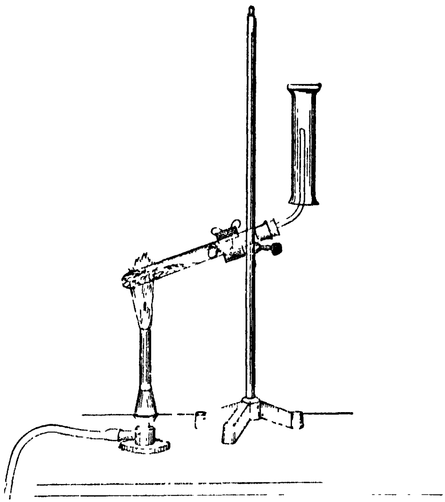


FIG. 21

closed with cardboard or a loosely fitting cork. When the gas is coming out from the mouth of the test-tube, you should remove the delivery-tube. Now close the test-tube with a tightly fitting cork, and collect another test-tube or two in the same way.

Put into the ammonia fumes a glass rod on which is a drop of strong hydrochloric acid. What effect is produced? Try to light the gas as it escapes from the mouth of the delivery-tube. Does it burn? What effect does

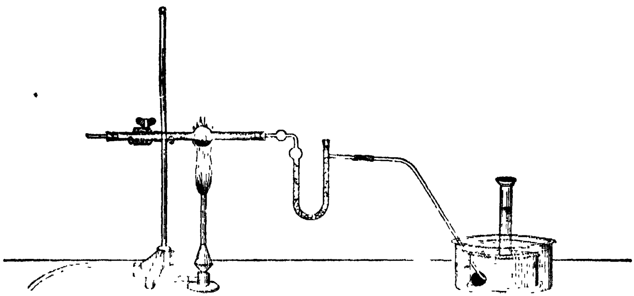


FIG. 22

it have on the flame of the taper applied to it? Ammonia burns in pure oxygen, and if you have some oxygen at hand you should try the experiment, and compare the appearance of the flame with that of hydrogen. Connect the delivery-tube with a glass tube containing black oxide of copper, as shown at the left of Fig. 22. The other end of the tube is joined with a U-tube and delivery-tube. Heat the copper oxide. What do you notice in the U-tube? When enough gas has been collected in the cylinder, test it by smell and by a lighted taper. Is it ammonia? What gas is it like? What change has taken place

in the copper oxide? What did the copper oxide give to the ammonia? What must have been in the ammonia to produce the substance in the U-tube? Of what two elements is ammonia composed? Is it a compound of these two elements, or is it a mixture?

Now hold, mouth downward, one of the test-tubes of ammonia that you collected. Open it and put a lighted taper into the gas. Is it combustible? Is it a supporter of combustion?

Put another test-tube, mouth downward, into the pneumatic trough containing water. Holding the tube firmly, remove the cork. What happens? Why did you not attempt to collect ammonia over water in the same manner as oxygen and hydrogen are collected?

Statement of Occurrence, Preparation, and Properties of Ammonia. — Why is ammonia sometimes called volatile alkali? It was at one time largely made from horns of the hart and is known under the name "spirits of hartshorn." The most of it is now made when coal is distilled in making coal gas. It is formed in the decay of most animal tissues, and is found in sewage. Hence, when water is found to contain more than the very smallest traces of ammonia, it is considered unfit for drinking purposes, because the ammonia probably comes from sewage or from decaying matter.

Ammonia is a very important fertiliser, because it provides nitrogen for plants which are, for the most part, unable to take it from the air. The fertiliser used is not pure ammonia, but its compound with sulphuric acid, very similar in appearance to the ammonium chloride with which you have experimented.

It must not be considered that ammonia exists as such

in coal or in horn and is merely driven out by heat. It is made from the nitrogen and hydrogen compounds that exist in these substances. When they are heated, the nitrogen and hydrogen compounds decompose and the two elements combine in the process of distillation, though free nitrogen and hydrogen gases do not readily combine to form ammonia. In ammonium chloride ammonia may be said to exist ready formed. When ammonium chloride is heated it breaks up directly into ammonia and hydrochloric acid, two gases which can be separated from each other at least partially, but if allowed to cool without being separated reunite to form ammonium chloride again. When substances decompose in this way by heat alone, recombining on cooling to form the original substance, they are said to *dissociate*.

Some of the properties of ammonia you already know. What reason have you to believe that it is lighter than air? It is only a little more than half as heavy as air. Though — like hydrogen, oxygen, and nitrogen — it is colourless, it is neither tasteless nor odourless. It is, as you found, very soluble in water, which dissolves, at the ordinary temperature, not far from one thousand times its volume of the gas. The solution of ammonia in water is called ammonia water or ammonia liquor.

When ammonia water is boiled long enough, all of the ammonia can be driven off, the water left behind containing no ammonia. During the process, some of the water is volatilised with the ammonia. Gases which are easily dissolved are usually easily condensed. Ammonia can be condensed by a pressure of seven atmospheres at the ordinary temperature or without additional pressure by cooling to $-38°$ C. Liquid ammonia (which must be

distinguished from ammonia liquor) is used for refrigerating purposes, such as making artificial ice, because it absorbs heat in evaporating. In some apartment houses in New York and elsewhere, the ammonia is used to cool a liquid (such as calcium chloride solution) which does not freeze so easily as water. This liquid passes through pipes to the different refrigerators all over the building; so that we may say that cold is supplied to the tenants just in the same way as heat is. It seems rather curious at first sight that in order to provide the low temperature a steam engine should be used, but it is evident that the liquid ammonia that evaporates must be recondensed, and so requires work to be done upon it.

Liquid ammonia does not produce so low a temperature as liquid air, and hence is not so powerful a cooling agent, but it is more easily manufactured and more easily preserved than liquid air. On the other hand, on account of its smell, it must be kept in closed vessels, whereas, of course, liquid air may be left open.

The chemical properties of ammonia depend partly on its being a compound of nitrogen and hydrogen. It burns in oxygen because hydrogen has so great an affinity for oxygen that the heat produced can keep the ammonia at the *kindling* or *ignition* temperature. When substances combine readily, they produce heat in combining, but if the substances are kept cold enough they will not combine. Phosphorus, though it burns so readily, will not combine with oxygen if it is kept cold; but if one part of it becomes hot enough to combine with oxygen, so much heat is produced that the next part of the phosphorus is made hot enough to combine with the oxygen, that is, reaches its *kindling* temperature. In the case of ammonia, when

it is lighted in an atmosphere of pure oxygen at the ordinary temperature, the heat produced by the burning of the hydrogen is enough to heat the next part of the ammonia to the kindling temperature, and so a jet of ammonia once lighted continues to burn in oxygen. Air contains so much nitrogen that the heat produced by the union of the hydrogen in the ammonia and the oxygen of the air is not enough to raise the temperature of the ammonia and the neighbouring air high enough to cause them to combine, and so a jet of ammonia does not continue to burn in air unless a flame is constantly applied. A *mixture* of nitrogen and hydrogen in exactly the same proportion as they exist in ammonia would continue burning in air if once lighted, thus showing that heat must be required for the decomposition of ammonia into its elements, and since some heat is required for decomposition of the ammonia, the temperature caused by the burning of the hydrogen is not so high as when all the heat is applied to raising the temperature of the gases. When ammonia burns, the main part of the combustion is due to the hydrogen uniting with oxygen; almost all of the nitrogen being set free, though a very small portion may combine with oxygen.

The weight of nitrogen in ammonia is to the weight of hydrogen in the ratio of 14 to 3. The experiment to prove this is not very easy to carry out, but it is merely a modification of the one you did in passing ammonia over hot copper oxide.

Ammonia gas may be decomposed by electric sparks in a eudiometer, and the volume of the nitrogen and hydrogen produced is twice that of the ammonia. By putting in enough pure oxygen with the gases and passing an

electric spark, the hydrogen is all used up and it is found that the volume of the nitrogen left is just one-quarter that of the nitrogen and hydrogen together, and therefore the hydrogen must be three-quarters; in other words, the volume of the hydrogen obtained from ammonia is three times that of the nitrogen.

There are other chemical properties of ammonia that could not be predicted from its composition any more easily than its odour could. Ammonia combines readily with acids producing substances in many respects like common salt, and hence called salts. This was what you saw happen when you put the rod moistened with hydrochloric acid into the fumes of ammonia. The two substances, the gaseous hydrochloric acid given off from the drop of solution, and the gaseous ammonia, united to form a white smoke of solid ammonium chloride.

CHAPTER V

CARBON DIOXIDE AND MONOXIDE

Effect of the Breath on Lime-water. — EXPERIMENT 25. Pass the breath from the lungs, for two or three minutes, through about 10 c.c. of baryta-water, or about 100 c.c. of lime-water. What change do you notice in the solution? A solid thus formed from a clear solution by the addition of another clear solution, or a gas, is called a *precipitate*, because if allowed to stand it would precipitate, or settle to the bottom. (If you have both lime- and baryta-water, you can tell by evaporating equal quantities of each, — a few drops, for instance, — why more lime-water is necessary than baryta-water.) Filter through a small filter-paper so as to obtain the precipitate on the paper. Transfer this paper to a small test-tube and pour upon it a few drops of hydrochloric acid. When bubbles of gas are set free as in this case, the substance is said to *effervesce*, or *effervescence* is said to *take place.* Into the test-tube put a burning match. Does it go out, or does it continue to burn? In the mouth of the test-tube hold a glass rod on which is a drop of lime-water or baryta-water. What evidence have you that the gas which you obtained by putting hydrochloric acid on the precipitate is the same as that in the breath which produced the precipitate?

Leave lime- or baryta-water open to the air. Does it turn cloudy as soon as when you breathe through it?

What does your result prove about the relative quantity of the gas in the air, and in the breath when it comes from the body? What two elements did we find are contained in this gas? See page 31. Which of them is supplied by the air? Where did the other element come from in the experiment that you have just performed?

When we breathe, part of our tissues are burned, but the burning is slow and the temperature is not high. In fever, the burning is more rapid, and the temperature rises. When we take violent exercise, the temperature also rises somewhat, but not as in fever, because the heat is diminished by the perspiration produced.

Was the volume of the precipitate that you have been experimenting with so great as that of the gas obtained from it? When this gas was first investigated by Black, in 1755, he called it "fixed air," because it appeared to be *fixed* in chalk in the solid state. Black made his experiments with chalk. You may use chalk or marble or ordinary limestone.

Preparation of "Fixed Air" and Experiments with the Gas. — EXPERIMENT 26. Put a number of small lumps of marble (chalk or limestone) into a flask fitted up as for hydrogen (page 19). Cover the marble with water and pour through the thistle-tube some hydrochloric acid, till you see the gas coming off pretty rapidly. Collect over water a number of cylinders of the gas. Remove them from the water, keeping them covered with glass plates or cardboard.

Open one cylinder, mouth upward, and another mouth downward, and after a minute thrust a burning taper into the two cylinders. What does this experiment prove about the weight of fixed air as compared with that of

atmospheric air? Light the taper again and put it into the cylinder in which it was extinguished. Notice this time whether the taper is completely extinguished or whether the wick is left glowing.

Siphon the fixed air from another cylinder and let the gas as it comes out of the siphon flow upon the flame of a candle. What happens to the candle? The siphon of the gas needs to be started just as a siphon of water would need to be started, and this may easily be done by sucking the air out of the tube. When doing so you will learn the taste of the gas. What reason have you for thinking that "soda water" may contain fixed air? If it does, what reason have you for considering that more fixed air can be dissolved in the water in the bottle where it is under pressure, than can be dissolved in water open to the air?

Fixed air is sometimes produced in old wells, and as the gas is poisonous, such wells are tested, if one wishes to go down into them, by lowering a lighted candle to the bottom. How is this a test?

Half fill another cylinder of the gas with water, cover air-tight with the hand, and shake vigorously for a minute or two. Have you any evidence from the feeling of your hand that the gas has been partly absorbed by the water? Put the mouth of the cylinder under water in the pneumatic trough and remove your hand. What evidence have you now that the gas was dissolved to some extent in the water?

Place a piece of both red and blue litmus-paper in a cylinder of fixed air. Is it acid, alkaline, or neutral?

In addition to fixed air there is another compound of oxygen and carbon. Since the proportion of oxygen to carbon

in fixed air is twice that in the other compound, the former is carbon *dioxide* and the latter carbon *monoxide.*

Carbon Monoxide

Laboratory Method of Preparation of Carbon Monoxide and Experiments with the Gas. — If carbon dioxide is passed over red-hot iron, it loses some of its oxygen and becomes carbon monoxide, while an oxide of iron is formed, just as

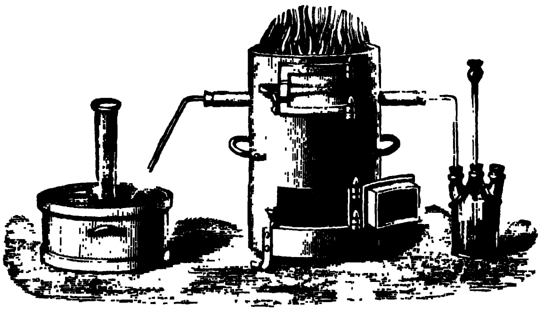


Fig. 23

when steam is passed over red-hot iron. A method of operation which might be used is shown in Fig. 23. The volume of the monoxide is equal to that of the dioxide from which it was obtained. When carbon monoxide is required in the laboratory it is not usually prepared in this way, but by heating oxalic acid with strong sulphuric acid.

Oxalic acid is a solid, composed of carbon, oxygen, and hydrogen, in such proportions as to form water, carbon monoxide, and carbon dioxide ; and all it needs is to be broken up in the right way, in order to obtain these three. Strong sulphuric acid has such a great affinity for water that when put on many substances that seem quite dry, but

that contain hydrogen and oxygen, it abstracts water from the compound. The chemical reaction is probably more complex than here indicated, but for our purpose we may rest content with the above explanation. The *fact* is, that when oxalic acid is heated with strong sulphuric acid, the latter becomes diluted with water, and equal volumes of carbon monoxide and carbon dioxide are set free.

EXPERIMENT 27. Into a half-litre flask fitted with a thistle-tube and a delivery-tube, put about 20 grammes of oxalic acid and cover it with strong sulphuric acid. Place the flask on wire gauze on the ring of a retort stand. Arrange two *wash bottles* half filled with a solution of caustic potash, so that they may be connected with the delivery-tube of the flask. In one form of wash bottle, the bottle is fitted with two tubes, the longer of which dips beneath the surface of the liquid in the bottle and serves to bring the gas from the generating apparatus while the shorter tube is well removed from the liquid and serves as a means of escape for the gas after its impurity has been absorbed by the liquid. Two wash bottles are used, lest one should not absorb all of the impurity. (Figure 24 shows such an apparatus.) Heat the flask gently, moving the flame about under it. How can you tell when the gas begins to come off? When you think that there is some escaping from the delivery-tube, hold a rod with a drop of lime-water or baryta-water on it in the stream of the escaping gas. What change is there in the lime-water? What does this show? Be careful not to inhale much of the escaping gases. Now join up the flask with the wash bottles placed so that the gas passes through one and then through the other. The gas which escapes from the second wash bottle can be collected in cylinders over water

as usual. What is there besides the liquid in the flask and wash bottles when you begin your experiment? Why do you not begin to collect the gas at the very first? Before you begin to collect the gas, test what comes out from the wash bottle by a drop of lime- or baryta-water. Does the drop become clouded? What is absorbed by the caustic potash solution? Is the compound made by the action of

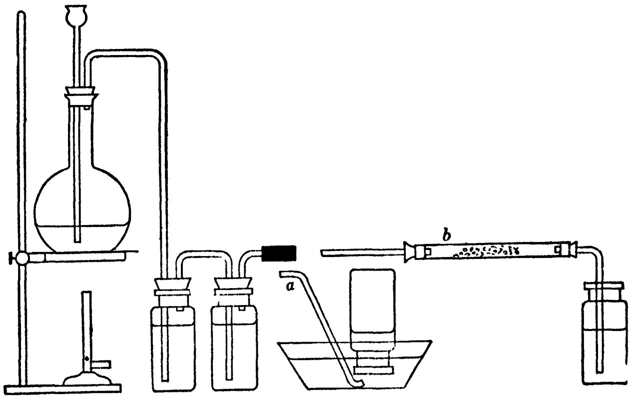


FIG. 24

carbon dioxide on caustic potash more or less soluble than the compound made by the action of carbon dioxide on caustic baryta (baryta-water) or lime?

When water has been kept back by sulphuric acid, and carbon dioxide by the caustic potash, what is still left to collect in the cylinders?

Collect several cylinders of carbon monoxide. To one add lime or baryta-water. If there should be no precipitate, apply a light to the gas in the cylinder. Is the gas combustible? Is it a supporter of combustion?

If the gas burns, notice the colour of the flame, and when

it goes out, shake up the lime-water in the cylinder and see if it becomes cloudy. What does carbon monoxide produce when it burns in air? If you got a precipitate when you first put in the lime-water, you should pour some caustic soda or potash into the cylinder, shake it up thoroughly with the gas, and transfer in the pneumatic trough to another cylinder and do the experiment as already described.

If you have a store of oxygen, fill a cylinder one-third with oxygen and then add carbon monoxide till the cylinder is full of gas. Remove the cylinder and carefully apply a lighted taper. You should have a violent explosion. Instead of oxygen you may use air, filling five-sevenths of the cylinder with air and two-sevenths with carbon monoxide. The tube *b* in the figure contains copper oxide which is supposed to be heated while carbon monoxide is passed over it. What liquid is supposed to be in the bottle, and what does the experiment show?

Shake up carbon monoxide with water as you did carbon dioxide. Is it more or less soluble?

Statement of Occurrence and Properties of Carbon Dioxide and Carbon Monoxide. — It will be convenient to discuss carbon dioxide and carbon monoxide together, comparing and contrasting them.

Since carbon monoxide burns in air, it is natural to suppose that there would not be much of it found free in the atmosphere. On the other hand, carbon dioxide is produced when all ordinary fuels burn and when all animals breathe, and so naturally exists in the atmosphere at all times. There are about four volumes of carbon dioxide in ten thousand volumes of air, and there would be a larger amount but that plants decompose it, taking

in carbon dioxide and sending out oxygen in somewhat the same way as animals inhale oxygen and exhale carbon dioxide.

Carbon dioxide may be said to be found ready made in marble, chalk, and other kinds of limestone, and if these are heated strongly enough, carbon dioxide is given off and lime is left behind. It is in this way that ordinary *quick*lime is made. Some other minerals contain carbon dioxide, but limestone is the most important.

Of the properties of carbon monoxide and carbon dioxide you know something. They are both colourless; carbon monoxide has little odour or taste, but produces a very disagreeable sensation, resembling an odour and taste. Carbon dioxide has a slightly acid, pleasant taste and a slight odour. Both gases are usually spoken of as very poisonous, but they act in different ways. The blood is not a homogeneous liquid, that is, is not uniform. The redness is caused by small red bodies called red corpuscles floating in an almost colourless liquid. The red corpuscles contain a substance which takes up oxygen when blood passes through the lungs. The blood in this way becomes a brighter red. As it passes through the blood-vessels, the oxygen is given up to the tissues. Carbon dioxide is produced and combines with the corpuscles both red and white, but chiefly with the inorganic salts in solution, as well as with the aqueous liquid itself. As the blood passes through the lungs again, the carbon dioxide escapes from it and more oxygen is taken in. If an animal inhales too much carbon dioxide with the air, the carbon dioxide of the blood cannot escape from the lungs and so is carried along in the blood, and death will soon follow unless the animal is removed from the atmosphere contain-

ing the excess of carbon dioxide and put into an atmosphere with plenty of good oxygen, in which case it will probably recover in a short time and suffer no serious effects. There is a place in Italy where this experiment is said to be often performed. It is called the Grotto del Cano, because (the carbon dioxide being near the ground) dogs with their noses close to the earth are suffocated, while people can walk along uninjured, their heads being above the poisonous gas. Visitors are shown the experiment of leaving a dog in the grotto till he becomes insensible, and bringing him out in time to revive him. The action of carbon dioxide is therefore rather suffocating than poisonous. An investigator has stated that, provided a sufficient amount of oxygen is contained in the air, the presence of carbon dioxide is not injurious. Carbon dioxide from the breath contains organic matters that are hurtful and must be removed, and it is said to be owing to their presence and to the diminution of oxygen that headache and other poisonous effects have been attributed to carbon dioxide. Physiologists are not agreed on the matter, which needs further investigation.

The poisonous action of carbon monoxide is more serious. Carbon monoxide forms a compound with the part of the red corpuscles that should be oxidised by the air, and thus prevents the action of the oxygen. The compound is very firm, so that if an animal is taken out of an atmosphere of carbon monoxide into the air, the oxygen still cannot act on these corpuscles, and the only chance of recovery is that there are enough corpuscles unacted upon to carry on the processes of life. An atmosphere of pure oxygen is more effective than air in its action on the blood, and is thus to a certain extent an antidote to poi-

soning by carbon monoxide. Carbon monoxide is by far the more dangerous of the two gases, and it is nearly always produced to some extent where coal is burned (the blue flames seen in coal fires being due to its combustion). It is said that red-hot iron allows the gas to pass through it, and that therefore red-hot stoves are unhealthy, but it is possible that the bad effects of hot stoves are due to other causes.

Carbon monoxide is slightly lighter than air, being of the same density as nitrogen, while carbon dioxide is about one and a half times as heavy as air.

Carbon dioxide at the ordinary temperature is dissolved by about its own volume of water, while carbon monoxide is, like hydrogen and oxygen, very slightly soluble.

Carbon dioxide is, as might be expected, the more easily condensed, becoming liquid at 15° C. when subjected to a pressure of fifty-two atmospheres and liquefying at ordinary pressure if cooled below − 80° C. Carbon monoxide is not liquefied at all at the ordinary temperature, no matter what pressure is employed. When liquefied by very intense cold the liquid boils at − 190° C., which is almost the same temperature as that at which nitrogen boils.

The chemical properties of the two gases are very different. Carbon monoxide burns in air, to form carbon dioxide, while naturally the latter does not burn in air, else it would not be the product of the combustion of the monoxide. Carbon dioxide combines with alkalis in aqueous solution, whereas carbon monoxide does not. Liquid carbon dioxide is sold in strong iron cylinders, and is used, among other things, for making soda water.

CHAPTER VI

ACTION OF HYDROCHLORIC ACID ON ALKALIS

Formation of Hydrochloric Acid. — EXPERIMENT 28. Test whether common salt is acid, alkaline, or neutral. Put a little salt into a test-tube, pour on it a few drops of strong sulphuric acid, and heat gently. What happens? Put a piece of moist litmus-paper into the mouth of the test-tube without allowing it to touch the sides, lest it should get a little of the sulphuric acid on it. Is there any indication that a gas is coming off? If so, is it acid, alkaline, or neutral? In another test-tube heat some sulphuric acid alone. In neither case should the test-tube be heated so strongly that you cannot keep your hand on the heated part when you remove it from the flame. Is there any effect on the litmus-paper held at the mouth of the test-tube containing sulphuric acid alone? Does sulphuric acid volatilise at the temperature which you have used? What evidence is there that when sulphuric acid is put upon the neutral substance, salt, an acid different from sulphuric acid is produced?

The substance formed by the action of oil of vitriol (sulphuric acid) on common salt was once called "spirits of salt." It is now called hydrochloric acid. Hold a glass rod, with a drop of water on it, in the mouth of the test-tube in which hydrochloric acid is being produced. After a few seconds, taste the drop. What evidence have you that water dissolves spirits of salt? What effect

would you expect a drop of the solution to have on litmus-paper? You remember that the volatile alkali ammonia was produced by the action of a fixed alkali, lime, on a salt, sal-ammoniac. Is sulphuric acid or hydrochloric acid the more volatile? There are very few volatile alkalis in common use, but there are a number of volatile acids. What hint have you of a possible method for getting a volatile acid from a salt? It is not well to jump too rapidly to conclusions; but whenever you are in doubt as to how to produce an acid from a salt, you should remember how hydrochloric acid is obtained from common salt, and consider whether there is any objection to using a similar method for the acid which you wish to obtain.

There are many properties of hydrochloric acid that we shall have to consider later, but just now we shall investigate the action of hydrochloric acid on alkalis such as caustic soda and caustic potash.

Addition of Hydrochloric Acid to Caustic Soda. — EXPERIMENT 29. Into a porcelain evaporating dish put a piece of caustic soda about the size of a small bean. Pour on it two or three times its own volume of water and allow it to dissolve. What change do you notice in the temperature? Now very carefully add a few drops of strong hydrochloric acid solution, allowing it to run down the side of the dish, not pouring it directly on the caustic soda. What evidence have you that the hydrochloric acid and the caustic soda act very energetically on each other? Continue adding hydrochloric acid till there is no further action. What evidence have you that hydrochloric acid has made the substance less soluble? Evaporate till the solid is perfectly dry. Is the substance left behind caustic soda? What does the *residue* after evaporation (the sub-

stance left behind when all the liquid was evaporated) taste like?

An experiment such as you have now performed is called a *qualitative* experiment, because you have examined the *qualities* of the substances used and the substance produced. You have taken no particular care about *quantities*. But in chemistry it is often very important to know something about quantities, and our knowledge is very imperfect unless we have such information. Let us endeavour to find out whether there is any definiteness about the quantity of hydrochloric acid which can be used up by a given amount of caustic soda, or whether the quantity varies.

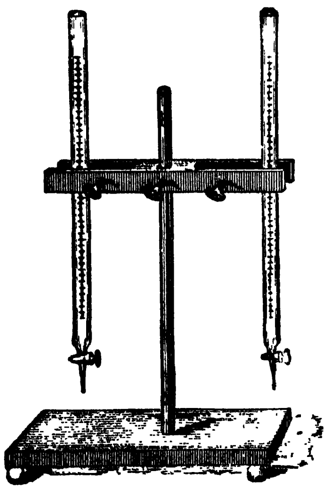


FIG. 25

Quantitative Experiments with Caustic Soda and Hydrochloric Acid; Burettes. — EXPERIMENT 30. Dissolve 4 grammes of caustic soda in 200 c.c. of water and stir so that the solution will be uniform. In another vessel mix thoroughly 25 c.c. of strong hydrochloric acid solution and 375 c.c. of water. Thoroughly clean a burette (a graduated glass tube such as those represented in Fig. 25). The burette must not be greasy inside, nor must drops remain on the walls when the contained liquid runs out. It may be necessary to rinse the tube with strong caustic soda solution or with nitric

acid, or, perhaps still better, with a solution of potassium dichromate and sulphuric acid. It must finally be thoroughly washed with water. Allow the water to drain out, then put into the burette a little — about 10 c.c. — of the soda solution; let it run from end to end of the tube and drain out as well as possible. Then with the soda solution fill the burette to about the top of the graduation and clamp it in a vertical position. In the same way fill another burette with hydrochloric acid and clamp it in position. Run a little of the liquid from each of the burettes to make sure that the little delivery tube at the bottom is quite full of liquid and contains no air bubbles.

Now carefully read the burette containing the caustic soda. Reading the burette means finding the position of the top of the liquid. When you look at the top of the liquid you will see that it has a curved surface, and the best way to read is to find exactly at what place you see the lowest part of this curved surface (called the bottom of the meniscus). The burette is graduated from the top, and the burette you use should be graduated in c.c., which are numbered, and in tenths of a c.c., which are indicated by short lines. Suppose the top of the liquid is between the numbers 1 and 2, you look to see below which intermediate mark it is situated. You will easily be able to see *approximately* its position. Suppose it is somewhat below the seventh little mark. Then the reading is 1.7 +. But you should read it more closely, and to do so needs care. You must have your eye on a level with the bottom of the meniscus. In order to understand why, move your eye up and down and see if the reading appears to be the same in all positions of your

eye. The figure (Fig. 26) illustrates this point. You will probably need something dark just behind the burette to enable you to see the bottom of the meniscus plainly. You may now be able to judge pretty nearly how many tenths of the distance between the seventh and eighth division it is. Suppose it is six-tenths, the reading is 1.76. It is not very easy to read quite so closely, so that you may be satisfied if you can decide whether the reading is nearest 1.73, 1.75, or 1.77. You see now why it is so important that none of the liquid should cling to the sides of the tube when the solution is run out. You should wait a minute or so before taking a reading, until all of the liquid has drained down. Run 15 c.c. of the caustic soda solution into a porcelain dish, add a little litmus solution, and then after carefully reading the hydrochloric acid burette run in the acid. What change is there in the colour of the litmus just where the acid strikes the liquid in the dish? Does this colour remain or does it vanish? What difference is there in this respect between when you begin to run in the acid and after you have run in a considerable quantity? You wish to make the solution just neutral. What indication have you that you should add the hydrochloric acid more slowly after a while than you did at first? Why should you stir the liquid and add the acid drop by drop when you come near

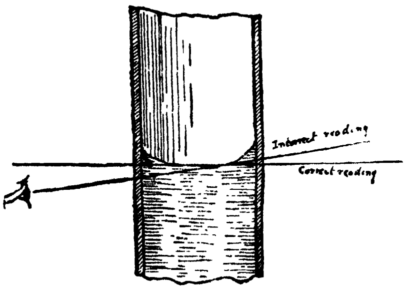


FIG. 26

the end? Each time you add a drop, notice the reading of the burette, not very accurately, but so close that you will have a pretty good idea how many hundredths of a c.c. there are in each drop. The size of drop varies with the burette. You will probably not succeed in hitting the neutral point exactly, but will overshoot the mark. If, however, you notice the reading of the burette each time you add a drop, you will have a pretty fair idea how much you *have* overshot the mark. If, for instance, when the burette read 20.60 c.c. the litmus was decidedly blue, and when you have added another drop you find the reading 20.66 and the litmus decidedly red, you can tell how much acid is required to within the limits of 0.06 c.c., and when you try a second time you endeavour to hit the mark more closely.

Having found how much acid is required to neutralise 15 c.c. of caustic soda, find out how much is required for 20 c.c. Is or is not the quantity of acid in the same ratio as the quantity of soda? It may be worth while to see whether the amount of acid required is the same if you dilute the caustic soda after putting it into the dish.

Weigh a small porcelain dish, put in 20 c.c. of caustic soda, and exactly neutralise with hydrochloric acid. Then evaporate to dryness and weigh again. What is the solid residue? How much does it weigh? Take another 20 c.c. of soda also in a weighed porcelain dish, add considerably more acid than is necessary to neutralise it, evaporate to dryness, and weigh. Can you get more salt, or can you not, by adding the larger quantity of acid? Is the residue this time alkaline, neutral, or acid? If you have a given quantity of salt, would it be possible for you to calculate how many c.c. of your caustic soda solution

and of your hydrochloric acid would be necessary to produce it, or is such a calculation impossible?

Quantitative Experiments with Caustic Potash and Hydrochloric Acid.—EXPERIMENT 31. Dissolve 4 grammes of caustic potash in 200 c.c. of water. Every c.c. of the solution will now contain as much caustic potash as the other alkaline solution contained of caustic soda. Put some of the solution into a burette. You may use the one you had for the soda, cleaning it out and rinsing it with a little of the potash solution. Find out how much hydrochloric acid is required to neutralise 15 c.c. and 20 c.c. of this solution. Is the amount of acid in the same ratio as the quantity of caustic potash solution? Does it require exactly the same amount of hydrochloric acid to neutralise 20 c.c. of caustic potash as of caustic soda? If not, what is the ratio between the amounts? Take 20 c.c. of caustic potash in a weighed porcelain dish, neutralise, evaporate to dryness, and weigh. Take another 20 c.c. of potash, add much more than enough acid to neutralise, evaporate to dryness, and weigh. How do the weights compare? What happens to the extra acid that was added in the second case? Is the weight of the salt obtained from 20 c.c. of the caustic potash solution equal to, less than, or greater than the weight of the salt obtained from 20 c.c. of the caustic soda solution?

The experiments that you have done should enable you to answer the following question; but if not, you had better try the direct experiment. Will 20 c.c. of hydrochloric acid need a greater or less weight of caustic potash than of caustic soda exactly to neutralise it? Is the weight of caustic potash, *equivalent* to a given weight of hydrochloric acid, greater or less than the weight of caustic

soda, equivalent to the same given weight of hydrochloric acid? This question is frequently put in the shorter form: Is the equivalent of caustic potash greater or less than the equivalent of caustic soda?

If other acids were used instead of hydrochloric acid, corresponding experiments might be carried out.

CHAPTER VII

LAWS OF CHEMICAL COMBINATION AND THE ATOMIC THEORY

You have now become acquainted with a number of chemical substances, having passed from very familiar ones to others not so commonly known. You have obtained a few quantitative results, and in some cases when you did not yourself perform the experiment you were told what has been proved experimentally by others.

Quantitative Results Recapitulated. — Water consists of hydrogen and oxygen, the volume of the hydrogen being twice that of the oxygen, while on the other hand the weight of the oxygen is eight times that of the hydrogen.

The zinc used for making hydrogen is approximately six-tenths the weight of the strong sulphuric acid required. The weight of potassium chloride obtained by heating potassium chlorate is approximately six-tenths that of the chlorate. Ozone is one and one-half times as heavy as the same volume of oxygen. Ammonia is composed of hydrogen and nitrogen, the volume of hydrogen being three times that of the nitrogen, while the weights are in the ratio of 3 to 14. Carbon dioxide has twice the quantity of oxygen for a given amount of carbon that carbon monoxide has. The quantities of hydrochloric acid needed to neutralise soda and potash you have investigated pretty thoroughly

Another experiment, in which considerable accuracy

may be attained, will give you further confidence in the quantitative results of chemistry.

Quantitative Experiment; Experimental Errors. — EXPERIMENT 32. Weigh carefully about 2 grammes of perfectly dry potassium chlorate. It is necessary that you should note exactly the weight, but not that it should be exactly 2 grammes. Mix it with about half its weight of perfectly dry manganese dioxide; introduce the mixture into a dry test-tube and weigh. Heat the mixture until all of the oxygen in the chlorate is given off. When the tube is cool, weigh it again. To what is the loss of weight due? Why was it so necessary to have everything dry?

There are always errors in carrying out an experiment, errors called *experimental errors*. The amount of error is in some cases small, if the experiment is easy and the experimenter is very careful. In some cases the experimental error is large. In the above experiment one member of a class experimenting might weigh the chlorate inexactly, another might lose a little of it after it was weighed, a third might not have had it perfectly dry, a fourth might not heat till all of the oxygen was driven off, a fifth might have a little of the mixture thrown out of the tubes by the oxygen coming off rapidly, and a number of other errors might occur. Some of the errors might make the amount of oxygen appear greater than it should, others would make it appear less. But if the average of the results obtained by ten or a dozen experimenters, who had exercised a reasonable amount of care, were taken, the probability is that the result would not be far wrong. In this case the amount of oxygen should be nearly 39.2% of the original chlorate. What will be the amount of chloride left?

The Law of Definite Proportions. — Your experiments have gone a certain distance to prove that a chemical compound always has the same composition. One sample of potassium chlorate does not contain 39.2% of oxygen, and another sample 41%. A certain amount of common salt is not made to-day from 10 grammes of caustic soda, and to-morrow from 10.5 grammes.

The statement that the composition of compounds is invariable or always the same is usually called the first chemical law, or **The Law of Definite Proportions.** Between the years 1799 and 1806 there was a great controversy, chiefly between two French chemists, as to whether this statement were true, so that it has been very carefully tested.

The Law of Multiple Proportions. — You found that there are two oxides of carbon, — carbon monoxide and carbon dioxide. Carbon monoxide contains 57.14% of oxygen and 42.86% of carbon. Carbon dioxide contains 72.73% of oxygen and 27.27% of carbon, that is, 42.86 grammes of carbon are combined with 57.14 grammes of oxygen in carbon monoxide, and 27.27 grammes of carbon are combined with 72.73 grammes of oxygen in carbon dioxide. If the calculation be made, it will be seen that in carbon monoxide 1 gramme of carbon is united to 1.33 grammes of oxygen, and in carbon dioxide 1 gramme of carbon is united to 2.66 grammes of oxygen.

Dalton described several cases like this, between the years 1803 and 1807, and he made the statement that is often called the second chemical law, or **The Law of Multiple Proportions.** This statement is that when two elements combine with each other in more than one proportion by weight, the quantities of one of the elements which com-

bine to form two or more compounds with a given quantity of the other element stand in simple relations to each other. For instance, a given quantity of carbon unites with a certain definite quantity of oxygen or with twice that quantity, and not with 1.6354 times that quantity. There is a sudden jump from the given amount of oxygen to double that amount. In the same way hydrogen unites with eight times its weight of oxygen to form water, and with sixteen times its weight to form hydrogen peroxide. We found that there are two oxides of iron — one, red hematite, which is non-magnetic, and another which is magnetic. The oxygen is not twice as much in one case as in the other, but the proportions are simple.

The amount of oxygen in the air varies between the limits 20.84% and 20.99% by volume. Is it probable that air is a mixture of oxygen and nitrogen, or a compound? *

The Atomic Theory; Dalton's Symbols. — Dalton set himself to devise some theory to account for the fact that elements unite in this simple way, that a compound is always of a definite composition, and that elements do not unite in haphazard proportions. He suggested the atomic theory. This theory is that all substances are made up of innumerable small indivisible particles, called atoms (from the Greek word meaning incapable of being cut). These particles are far too small to be visible through a microscope. We do not know their shape, and our knowledge of their size and weight is very vague. In the case of elements all the atoms are alike; compounds are made up of different kinds of atoms. Though we do not know the actual weight of the atoms, we know the ratio between the weights of the different kinds of atoms.

Dalton used certain symbols to represent atoms of dif-

* See Appendix B, which should be carefully read before proceeding.

ferent elements, and when he wished to represent a compound he put the proper symbols together. Oxygen was represented by the symbol ○, hydrogen by ⊙, nitrogen by ⦶, carbon by ●. Carbon monoxide was represented by putting the symbol for one atom of carbon beside that for one atom of oxygen, thus, ●○, while carbon dioxide was represented thus, ○●○.

It is easily seen that the smallest possible quantity of carbon monoxide would consist of one atom of carbon and one atom of oxygen, for this amount of carbon monoxide could not be divided without breaking up the substance into its elements. It would be impossible to add oxygen to this smallest quantity of carbon monoxide except by adding one or more atoms of oxygen. One atom of oxygen can, in fact, be added, forming carbon dioxide; and the smallest quantity of carbon dioxide contains two atoms of oxygen for one of carbon. Any large quantity of carbon monoxide or of carbon dioxide is merely made up of innumerable numbers of these smallest quantities, and so the percentage composition of a large quantity is exactly the same as of the very smallest quantity that can exist. This smallest quantity is called a *molecule*. A molecule is the smallest quantity of a substance that can exist in the free state or, in other words, that can have a separate existence.

Dalton considered water to consist of one atom of hydrogen and one atom of oxygen, and represented it by the symbol ⊙○. But when sodium acts on water, one-half of the hydrogen is set free, and one-half of it, as well as all of the oxygen, combines with the sodium. The simplest explanation is that each molecule of water contains two atoms of hydrogen and one atom of oxygen.

The atom of oxygen and one of the atoms of hydrogen unite with an atom of sodium to form a molecule of caustic soda, and one of the hydrogen atoms is set free. When a number of molecules of water are thus broken up, there is a corresponding amount of caustic soda produced and a quantity of hydrogen gas. There is no method known for dividing the oxygen in water into two parts, and so the molecule of water is considered to contain one atom only of oxygen. In hydrogen peroxide there is twice as much oxygen as in water, and the oxygen can be divided into two parts; so the molecule of hydrogen peroxide is considered as made up of two atoms of hydrogen and two atoms of oxygen.

The atom is the smallest quantity of an element capable of entering into chemical reactions, but in many cases there is evidence that the smallest quantity of the element that is capable of a separate existence consists of *two* atoms and not of one. In such a case the *molecule* of the element consists of two atoms. In the case of some elements the molecule consists of more than two atoms, while in some cases the molecule consists of only one atom. You have not arrived at the stage when you can appreciate all the arguments, but you have learned one fact in favour of the view that the molecule of an element may contain more than one atom.

You remember that ozone is one and one-half times as heavy as oxygen. If there are the same number of molecules of ozone in a given space as there are of oxygen in the same space, each molecule of ozone must be one and one-half times as heavy as each molecule of oxygen. But a molecule of ozone cannot consist of an atom and a half, because an atom cannot be divided chemically; we can,

however, conceive that the molecule of oxygen is made up of two atoms of the element and the molecule of ozone of three atoms. As most of the common elements have two atoms in the molecule, it will be easiest to learn the exceptions as we meet them.

The Law of Gaseous Volumes. — Shortly after Dalton's law was announced and his atomic theory proposed, Gay-Lussac, a French chemist, made the statement frequently called the third chemical law, or **The Law of Gaseous Volumes.** The law states that when gases combine the volumes of the gases which enter into combination are very simply related to each other and to the volume of the compound produced, when the latter is a gas. For instance, two volumes of hydrogen unite with one of oxygen to form water; and if the temperature is high enough so that the water is in the form of vapour, its volume is exactly the same as that of the hydrogen. Three volumes of hydrogen and one of nitrogen are produced from two volumes of ammonia. Two volumes of carbon monoxide unite with one volume of oxygen to form two volumes of carbon dioxide. In some cases, though in none that we have dealt with, the volume of the compound is exactly equal to the sum of the volumes of the constituents, but in many cases there is contraction.

Avogadro's Law. — Dalton's law stated that there is a simple relation between the *number of atoms* of various gases taking part in chemical reactions; Gay-Lussac's law stated that there is a simple relation between the *volumes* of the gases; but the connection between the two laws did not make itself apparent to either of these chemists. In 1811, Avogadro, an Italian physicist, tried to explain Gay-Lussac's observation by an hypothesis, little regarded

for forty or fifty years, but now considered of the greatest importance. The statement of the hypothesis is usually called Avogadro's Law.

It is that equal volumes of gases under the same conditions of temperature and pressure contain the same number of *molecules*. We really made this assumption when discussing the number of atoms in a molecule of oxygen and in a molecule of ozone, because we assumed that there were the same number of molecules of ozone in a given space as molecules of oxygen in the same space. Since, as is well known, the volume of gases varies with change of temperature and pressure, it is evident why similar conditions of temperature and pressure are insisted on in Avogadro's law. In Gay-Lussac's law the same conditions are tacitly assumed.

If Avogadro's law is true, it is evident that if we know the relative density of two gases we shall know the relative weights of their molecules, because the density of a gas is the weight in unit volume, and unit volume of one gas contains just as many molecules as unit volume of another gas. The density of carbon dioxide is to that of carbon monoxide as 11 : 7, therefore the weights of their molecules are in the same ratio.

Avogadro's law makes no distinction between elementary gases and compound gases. The weight of a given volume of oxygen is *sixteen* times that of the same volume of hydrogen, and so the weight of the molecule of oxygen is *sixteen* times that of the molecule of hydrogen. The density of carbon monoxide is *fourteen* times that of hydrogen, therefore the weight of the molecule of carbon monoxide is *fourteen* times that of the molecule of hydrogen. The density of carbon monoxide is exactly the same as

that of nitrogen ; therefore the weight of the molecules of the two substances, one of which is an element and the other a compound, is exactly the same.

There has been a great deal of work done in order to determine the relative weight of the atoms. To determine this weight, it is necessary to know how many atoms there are in the molecule of the compound worked with. For instance, when Dalton thought that the molecules of water consisted of one atom of hydrogen and one atom of oxygen, he naturally said that the weight of the oxygen atom was eight times that of the hydrogen atom, because he knew that the weight of oxygen in water is eight times the weight of hydrogen. But now when we think that the molecule of water contains two atoms of hydrogen and one atom of oxygen, we say that the atom of oxygen weighs sixteen times as much as the atom of hydrogen, because one atom of oxygen weighs eight times as much as two atoms of hydrogen.

Hydrogen is the lightest substance known, and its atom is often taken as the unit, and we say that the atomic weight of oxygen is 16. In the same way we say the atomic weight of nitrogen is 14, of carbon 12, and so on for all the elements.

The Present Chemical Symbols.—Dalton, as we saw, used symbols for the atoms of different elements, but his symbols were soon replaced by the first letter of the Latin name of the element. Very often the Latin and the English names correspond, and so we have O for the atom of oxygen, H for the atom of hydrogen, N for the atom of nitrogen, C for the atom of carbon.

The names of a number of elements begin with the same letter, and in this case a second important letter

in the name is frequently added to the first to designate the atom. C stands for the carbon atom, it being a very important element, while Cl stands for the chlorine atom, Cd for the cadmium atom, and Cs for the cæsium atom. The Latin name for silver is *argentum*, and the symbol for the atom is Ag; the Latin name for gold is *aurum*, and the symbol for the atom is Au.

When the molecule of a compound is to be represented, the symbols of the atoms are put together; thus CO stands for the molecule of carbon monoxide. If there are two atoms of the same kind in the molecule, the figure is written at the right hand lower corner of the symbol for the atom; thus H_2O represents the molecule of water containing two atoms of hydrogen and one atom of oxygen. So also NH_3 represents a molecule of ammonia containing one atom of nitrogen and three atoms of hydrogen.

The weight of the molecule is got at by adding the weight of the atoms in it; the weight of the molecule of ammonia is 17, because the weight of the nitrogen atom is 14, and that of the three hydrogen atoms 3. The union of symbols to represent a compound is usually called a *formula*. As has been said, we do not know the actual weight of atoms or molecules, and so when we say that the weight of the molecule of ammonia is 17, or that the molecular weight of ammonia is 17, we merely mean that it is seventeen times the weight of the atom of hydrogen.

Symbols and formulæ always should mean a certain definite weight. When you see the formula NH_3, it should always convey the information that the weight of the nitrogen is to the weight of hydrogen as 14 : 3. It is a convenient theory that a large quantity of ammonia is made up

of an innumerable number of molecules, each of which contains an atom of nitrogen and three atoms of hydrogen. There are many facts which make this theory probable, and no facts are known inconsistent with it, but it is only a theory, and a fact to which the theory could not be reconciled would destroy the theory. But it is not a theory that 17 grammes of ammonia contain 14 grammes of nitrogen and 3 grammes of hydrogen, and, therefore, that 34 grammes of ammonia contain 28 grammes of nitrogen and 6 grammes of hydrogen, so the formulæ would remain if the whole *atomic theory* were proved incorrect. But until some fact is discovered to upset the theory, we may consider a formula as representing a molecule made up of atoms, as well as a certain definite weight made up of smaller weights. NH_3 represents a molecule or seventeen weights, usually *grammes*, of ammonia. But the formula NH_3 should not be used in general instead of the name ammonia.

TABLE OF ATOMIC WEIGHTS OF COMMON ELEMENTS*

NAME	SYMBOL	ATOMIC WEIGHT
Aluminium	Al	27.1
Antimony	Sb	120.2
Argon	A	39.9?
Arsenic	As	75.0
Barium	Ba	137.4

* This table is an abstract of one compiled by the International Committee on Atomic Weights in 1907. The atomic weight of oxygen is taken as 16, and the atomic weights of the other elements are compared with that. If hydrogen as unity were made the standard, the numbers representing the atomic weight would be slightly different.

Name	Symbol	Atomic Weight
Bismuth	Bi	208.0
Boron	B	11.0
Bromine	Br	79.96
Cadmium	Cd	112.4
Calcium	Ca	40.1
Carbon	C	12.00
Chlorine	Cl	35.45
Chromium	Cr	52.1
Cobalt	Co	59.00
Copper	Cu	63.60
Fluorine	F	19.0
Gold	Au	197.2
Hydrogen	H	1.008
Iodine	I	126.97
Iron	Fe	55.9
Lead	Pb	206.9
Lithium	Li	7.03
Magnesium	Mg	24.36
Manganese	Mn	55.0
Mercury	Hg	200.0
Nickel	Ni	58.70
Nitrogen	N	14.01
Oxygen (Standard)	O	16.000
Phosphorus	P	31.0
Platinum	Pt	194.8
Potassium	K	39.15
Selenium	Se	79.2
Silicon	Si	28.4
Silver	Ag	107.93
Sodium	Na	23.050
Strontium	Sr	87.6
Sulphur	S	32.06
Tellurium	Te	127.6
Tin	Sn	119.0
Zinc	Zn	65.40

The Kinetic Theory of Gases. — Closely connected with the atomic theory is the "Kinetic Theory of Gases."

It is considered that in the three states of matter, solid, liquid, and gaseous, the molecules are in motion, but the motion is different in character in each of these states.

In solids the molecules move through a limited space with a somewhat vibratory motion. In liquids they have a much wider range, but are always under the influence of other molecules. In gases the motion of each molecule is almost unaffected by the other molecules, except during collision. The motion is, therefore, for the most part in straight lines, just as would be the case with a few elastic balls flying about in a room. Such balls would hit against the sides of the room and rebound, and might occasionally hit each other, changing their course at each collision, but for the most part moving in straight lines. In gases the space between the particles is very large as compared with the size of the particles themselves, and therefore gases are easily compressed. The pressure of gases on the walls of the containing vessel is due to impacts of the particles, and just as a dozen balls flying about in a small room would hit the walls more often than the same number of balls in a large room, so the particles of a gas compressed into a small volume will give more impacts on the walls of the vessel, and therefore exert greater pressure. The higher the temperature, the more rapidly do the particles move, and therefore the greater pressure do they exert.

Long before the kinetic theory of gases was proposed, it had been discovered that gases exert a greater pressure when confined to a smaller volume and when raised in temperature, and the laws governing the change had been investigated. The theory explains not only these facts, but many others, and has so far held its ground.

CHAPTER VIII

COMMON SALT AND SOME SIMILAR COMPOUNDS

YOU have already performed some experiments with common salt. There are a number of other substances also called salts because they are in many respects similar to common salt. It will be interesting to study some of them, and the ones chosen are among those most similar to common salt, and are selected because through them we shall be led to the consideration of some substances of very great chemical interest and importance. The names of the salts are given in a footnote* so that the teacher may see at a glance what substances to provide, but the names are of no interest to us just now, and we shall designate the salts by numbers. We shall take them in groups of three, numbering them

1	2	3
4	5	6
7	8	9

the first on the list being common salt.

Experiments with Salts, etc. — EXPERIMENT 33. Taste a number of the substances, taking very small quantities. Several of them are medicinal, though common salt is the only one used with ordinary food. You have already treated common salt with sulphuric acid, but it will be

* The salts are sodium, potassium, and ammonium chloride, bromide, and iodide.

advantageous to repeat the experiment, for now you will be able to compare the reaction in that case with what takes place when the other salts are treated in the same way.

What evidence have you that a gas is produced when sulphuric acid acts on No. 1? What are the properties of the gas? See if you can discover whether it is heavier or lighter than air. To do this, hold the test-tube in which the gas is produced almost horizontal, and see whether the fumes rise or fall as they come from the tube. Draughts blowing through the laboratory may prevent the success of your experiment, but, if so, some other observations later on should decide the point. What about the colour and odour of the gas? Does it burn? Does it support the combustion of a match? What do you observe when you hold a drop of ammonia water on a glass rod near the mouth of the tube? Under what circumstances did you get a *similar* result before? The substance produced is the same in both cases. What is, therefore, the gas coming off from the test-tube?

Experiment with No. 2 in the same way, and answer the above questions in so far as they are applicable to it. Note particularly the differences between the action in the two cases.

Describe the action of No. 3 when treated in the same way.

Now see which of the other salts are similar to No. 1, which similar to No. 2, and which similar to No. 3, so far as the action of sulphuric acid is concerned.

EXPERIMENT 34. Mix a little powdered manganese dioxide with No. 1, and again treat with strong sulphuric acid. What effect has the manganese dioxide? How about the colour and smell of the gas?

Treat a little of No. 3, in the same way, with manganese dioxide and sulphuric acid. What evidence have you that the effect of the manganese dioxide is not so great as in the case of No. 1? Now try the same experiment with No. 2. Arrange the salts in the order in which the addition of manganese dioxide is effective, beginning with the case where the effect is greatest.

You should now have an idea what to expect, if you treat in the same way any of the other salts; for instance, No. 5 and No. 9. It may be well to see if your predictions are verified.

EXPERIMENT 35. Moisten the end of a platinum wire, dip it into No. 1, and hold it in the flame of a Bunsen burner or of an alcohol lamp. What is the colour of the flame? Test similarly all of the salts, finding out which give the same colour as No. 1. While doing so, make a note of the colour of the different flames. Of which salts is the flame colour most persistent? of which least persistent? Which substances are the most volatile?

Under what circumstances have you already had the same coloured flame as you have just obtained with No. 1? In the former experiments hydrogen was produced and was burning. What reason have you for thinking that the colour was not at that time due to hydrogen? If the colour was not produced by the burning of the hydrogen, what must have given it? What substance do you now know to exist in common salt? What other salts of the set contain the same element? Put a piece of glass, such as a tube or rod, into the flame. What is one of the constituents of glass? Watch the ordinary non-luminous flame and notice that you frequently get flashes of the same colour, due to dust floating about the laboratory.

You will thus see what a very small quantity of this particular element may be detected by the colour which its compounds give to the flame. The great Belgian chemist, Stas, succeeded in getting a flame not coloured by sodium, but to do so he had to wet the walls and ceiling and floor of the room, shut it up for three days so that the dust might settle, and he even then allowed no one to enter it but himself. What metal did you find before gives the violet flame that you have noticed in some of these salts?

Test any of the volatile salts by mixing it with a little lime, and smelling. What information have you obtained regarding its composition?

In what respects are Nos. 1, 2, and 3 alike? In what are they different?

In what respects are Nos. 1, 4, and 7 alike? In what are they different? Compare the other salts in the same way. Why were the salts arranged in three groups of three?

Common salt is, of course, the most important as well as the cheapest of all these salts, and we shall now find it advantageous to study more fully the compound obtained by the action of strong sulphuric acid upon it, though as you have seen, some others of the salts examined would give off the same gas if treated in the same way.

We shall soon be able to find out what else there is in common salt besides sodium, and soon after that the constituents of the other salts.

CHAPTER IX

HYDROCHLORIC ACID

Preparation of Hydrochloric Acid and Experiments with the Gas. — EXPERIMENT 36. Fit up a flask as in Fig. 27. Into the flask put a handful of common salt and cover it with sulphuric acid.* Attach a piece of rubber tubing to the delivery-tube so that connection may be made with a little glass tower, or some other vessel containing lime. You will soon be able to see the use of the lime. It is even better to perform the operation under a hood. Gently heat the

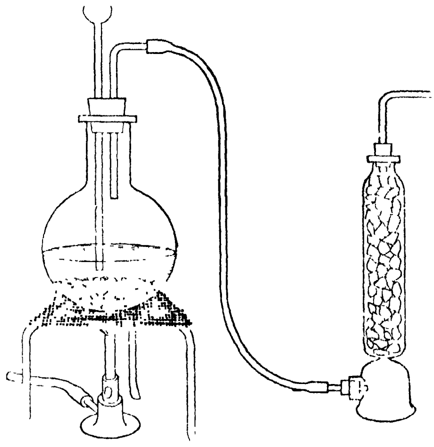


FIG. 27

* The strongest sulphuric acid might be used, but it is liable to produce frothing, and a better strength is that obtained by pouring eleven *volumes* of strong acid into eight of water. The solution must be allowed to cool before being put upon the salt. Cold acid of this strength does not liberate the hydrochloric acid gas, but gentle heating is sufficient to cause its evolution.

mixture of salt and acid till you see effervescence due to the formation of gaseous hydrochloric acid. Heat carefully, regulating the temperature according to the rapidity with which you desire the gas to come off. After the gas has come off long enough to drive the air out of the flask, disconnect the rubber tubing from the tower and attach to a glass tube having a jet. Pass the tube through a cork which can fit tightly into a bottle and push it down till it reaches the bottom of the bottle, placed mouth upward. While the bottle is being filled with the hydrochloric acid gas, the cork must be only loosely fitted into the bottle. Why? How can you tell when the bottle is full of gas? When it is full, draw out the tube that passes through the cork till it reaches halfway to the bottom of the bottle, disconnect the rubber tubing, which you should at once attach to the lime tower, push the cork tightly into the bottle, turn the latter upside down, putting the end of the tube several inches beneath the surface of water containing neutral litmus in the pneumatic trough or in a beaker. It may be well to support the bottle in the ring of a retort stand as shown in Fig. 28, since the experiment may take several minutes. Watch the water inside the tube. Why does it begin to rise? What happens when it reaches the top of the tube? What have you learned about the solubility of hydrochloric acid gas in water? What is its effect on litmus? Why would it be inadvisable to try collecting hydrochloric acid over water?

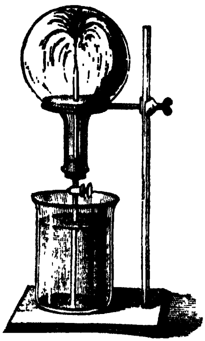


Fig. 28

EXPERIMENT 37. Arrange an apparatus as in Fig. 29, connecting the rubber tubing to the first of the series of bottles. Pass the gas for some time through the bottles. What evidence have you during the operation that the gas is dissolved by the water? After five or ten minutes disconnect and taste a very small drop of the liquid in each wash-bottle, beginning at the one farthest from the

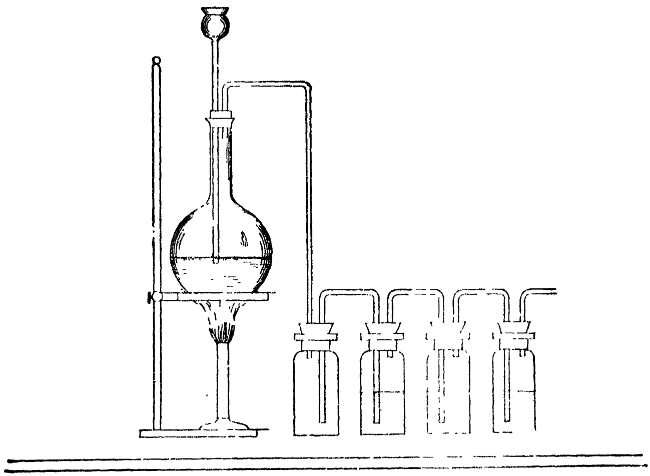


FIG. 29

generating flask. Which bottle contains the strongest solution of hydrochloric acid? Put some of the strongest solution into a porcelain evaporating dish and heat till at least three-quarters of the liquid is evaporated. Has the hydrochloric acid all gone off leaving pure water behind? Compare in this respect the evaporation of ammonia water and hydrochloric acid solution. A strong solution of hydrochloric acid is made commercially by absorbing the

gas in water. This absorption goes on in very large vessels, and the gas is produced in very large furnaces holding many tons of salt and sulphuric acid.

Gently pour some water upon the top of a concentrated solution of hydrochloric acid. A good way to do is to half fill a test-tube with the acid and to incline it toward the horizontal till the acid nearly comes out. You can then easily pour water on the top of the acid till the test-tube is three-quarters full. Does the water lie on the top of the acid, or does it sink through it? By using water containing litmus the position of the water may be made very distinctly visible. Which is the heavier, hydrochloric acid solution or pure water? How does hydrochloric acid solution compare in this respect with ammonia water?

Experiment 38. Collect a cylinder of the gas by downward displacement, and try whether a lighted candle or taper will burn in it. Also try the same experiment with burning sulphur and phosphorus. What is the result? Would you call hydrochloric acid a supporter of combustion? Into another cylinder of the gas plunge a deflagrating spoon containing burning sodium. What do you observe?

Experiment 39. Attach the rubber tubing to a tube similar to that which you used in Exp. 16, but instead of hematite put mercuric oxide into the tube. After the gas has been passing a few minutes without heating, what do you notice in the end of the tube farthest from the generating flask? What two substances have you already found to exist in mercuric oxide? What element does it supply in order to produce the moisture that you see on the glass of the tube? What element must be supplied

by the hydrochloric acid? What is one of the elements composing the white solid produced in the tube? Does the white substance consist of this element alone? If not, where has the rest of it come from? If there is any gas escaping from the tube, notice its colour and smell and test it with litmus-paper.

EXPERIMENT 40. Fit up a tube similar to that just used, putting in small pieces of manganese dioxide instead of mercuric oxide, and pass hydrochloric acid gas in the same way as before, gently heating the manganese dioxide. How far is the result similar to that obtained from the mercuric oxide? What is the colour of the gas passing out from the tube? Does it smell like hydrochloric acid? Smell very cautiously, indeed. What is its action on moistened litmus-paper? In the case of the action on mercuric oxide, what became of that part of the hydrochloric acid that is not hydrogen? What reason have you for supposing that when manganese dioxide is acted on by hydrochloric acid, some of this substance escapes and does not combine with the manganese?

Gases obtained by Electrolysis of Hydrochloric Acid Solution. — EXPERIMENT 41. Electrolyse a strong solution of hydrochloric acid in the same way as you electrolysed water in Exp. 8, or you may use a more elaborate apparatus such as that shown in Fig. 30. The electrodes should be of gas carbon, since chlorine acts on platinum. Gas carbon is a hard form of carbon found in the upper part of retorts in which coal is distilled. Test the colourless gas by applying to it a lighted match. What is the gas? What is the colour of the gas in the other tube? From its properties, what do you decide regarding the question whether you have already met this gas? If you

are told that the quantity of water in the electrolyte is just the same at the end of the operation as at the beginning, from what must this gas have come? On account of its green colour it is called chlorine, from the Greek word *chloros*. The gas now called chlorine was at one time

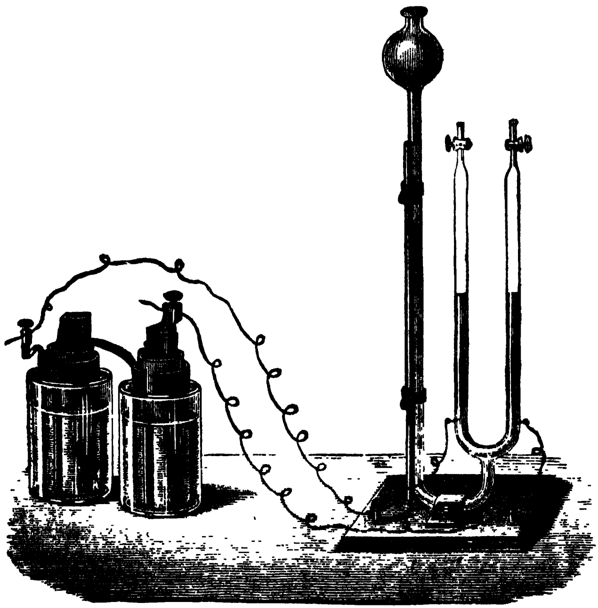


FIG. 30

considered a compound of hydrochloric acid and oxygen, and was called oxy-muriatic acid (muriatic acid being the earlier name for hydrochloric acid). It was, however, found impossible to get oxygen from it, and as chlorine has never been decomposed it is regarded as an element.

Hydrochloric acid is a compound of hydrogen and chlo-

rine, as we have seen, and since it is impossible to take away part of the hydrogen from hydrochloric acid without taking it all away, and in like manner it is impossible to take away part of the chlorine without taking it all away, the molecule of hydrochloric acid is considered to consist of one atom of hydrogen and one atom of chlorine, and is represented by the formula HCl.

EXPERIMENT 42. Put a piece of sodium (well cleaned from the crust which usually covers it) into a bulb tube as shown in Fig. 31; connect the tube with the generating

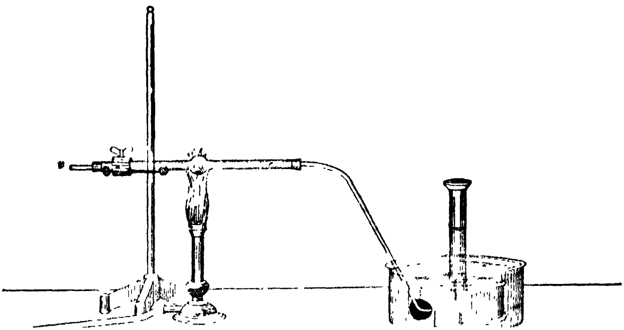


FIG. 31

flask and fit up the apparatus in such a manner that you can collect any escaping gas in a test-tube over the pneumatic trough. Let a current of hydrochloric acid pass in the cold till all of the air is driven out of the apparatus. How can you tell when this is the case? If you have been collecting the air in the test-tube, fill up the test-tube with water and put it in position again. Heat the sodium till it begins to burn, then remove the flame, as the action

goes on of itself. When the burning has ceased, continue to pass the hydrochloric acid a little longer, heating the tube where the sodium was. What is the gas collected in the test-tube? Test with burning match or splinter. What must have combined with the sodium? Wash out the substance in the bulb tube with a little water, and evaporate the solution till quite dry. Moisten with a drop or two of water, and test whether it is acid, alkaline, or neutral. It should be neutral. If it is acid, you have not dried it perfectly, and should heat it again. If it is alkaline, add a drop of hydrochloric acid solution till it reddens litmus-paper, and then evaporate off the acid. What does the substance taste like? What is the composition of the substance? The chemical name is sodium chloride.

Naming of Compounds containing Two Elements. — We found that an oxide is a compound of oxygen with another element (or a group of elements that acts like a single element), and so a chloride is a compound of chlorine and some other element (or group of elements that acts like a single element).

A compound of two elements is named by giving the name of one element, while the name of the other element is modified so as to end in the syllable *-ide*. Zinc oxide is a compound of the two elements zinc and oxygen, magnesium nitride is a compound of the two elements magnesium and nitrogen, and sodium chloride is a compound of the two elements sodium and chlorine. When one of the elements is a metal and the other is not a metal (in other words, is a non-metal), it is the latter which has the ending *-ide*. Some chemists prefer to modify the name of the first element as well, changing it from a noun to an

adjective, and to say sodic chloride instead of sodium chloride, and thus you will meet both forms of expression.

Suppose that enough hydrochloric acid had not been used to change all of the sodium into sodium chloride, what would have been found when the tube containing it was washed out? What reaction would it have to litmus? Suppose more hydrochloric acid used than necessary, what reaction would the solution have to litmus? Why were you told to continue passing the hydrochloric acid gas after the sodium had ceased to burn visibly?

You will now understand what was meant by saying that you cannot take away part of the chlorine from hydrochloric acid without taking away the whole. It did not mean that if you have a large quantity of hydrochloric acid gas nd a small piece of sodium, that the sodium would take up all of the chlorine from the hydrochloric acid; but any hydrochloric acid from which *the whole* of the chlorine has not been taken away, has been entirely unaffected and might as well not have been present. The sodium took all of the chlorine from so much of the hydrochloric acid as it acted upon and set free all of the hydrogen. This is different from the action of sodium on water; when sodium acts on water, it does not drive out all the hydrogen of the water that has been acted upon, but only one-half of it; and, as we saw, we consider the proper formula of the molecule of water to be H_2O, while we consider the proper formula of the molecule of hydrochloric acid to be HCl. In the same way we consider the formula for the molecule of sodium chloride to be NaCl.

The formula for the molecule of water is H_2O, representing that *two* atoms of hydrogen are united to one atom

of oxygen. But in red precipitate we assume that *one* atom of mercury is united to one atom of oxygen, and in lime that *one* atom of calcium is united to one atom of oxygen, hence their molecules are represented by the formulæ HgO and CaO. We are not perfectly sure that there is only one atom of each element in the molecule, but we *do* know that if our theory of atoms is correct, there are as many atoms of mercury as of oxygen in mercuric oxide, and as many atoms of calcium as of oxygen in calcium oxide, and we have no very good indication that there is more than one atom of each. We see then that in calcium oxide *one* atom of calcium unites with one of oxygen, whereas, in water, *two* atoms of hydrogen unite with one atom of oxygen. One atom of calcium, therefore, takes the place of, or is equivalent to, two atoms of hydrogen, and the equivalence of the calcium atom is two.

Valency. — We usually say that the *valency* of calcium is two, and we call the metal a *bivalent* element. *One* atom of chlorine unites with *one* atom of hydrogen, and we say that the valency of chlorine is *one*, or that it is a univalent element. One atom of oxygen unites with two atoms of hydrogen, and so oxygen is a bivalent element. If a bivalent element forms a compound with a univalent element, one atom of the former requires two atoms of the latter. If two bivalent elements unite, they can unite atom for atom. What is the formula of the molecule of calcium oxide? What of calcium chloride?

Beginners usually have difficulty in remembering the valency of the element, and so do not know how many atoms of each element to represent as existing in the molecule of the compound. The most important univalent metals are potassium, sodium, and silver, and the

formulæ of the chlorides* are KCl, $NaCl$, and $AgCl$. It may be assumed, in the meantime, that the remaining *common* metals are bivalent. Thus we have $ZnCl_2$, $CaCl_2$, $PbCl_2$, $MgCl_2$, and the corresponding oxides, ZnO, CaO, PbO, and MgO.

The metals that have other valencies will be learned as you proceed, and there is not usually much trouble with the non-metals.

You have had the opportunity to decide whether hydrochloric acid gas is heavier or lighter than air, but if you still do not know, you should before going on try some experiment that will determine the point.

Sodium Sulphate — Double Decomposition. — When the hydrochloric acid is all driven out from the mixture of salt and sulphuric acid, allow the flask to cool, and dissolve its contents in water, using as little water as possible, so that you may have some idea as to the solubility of the substance (that is, whether it needs much or little water to dissolve it), and that you may not have very much water to evaporate afterwards.

Evaporate the solution until some of the substance begins to crystallise, and allow to cool. Are these crystals like common salt in their taste and in the action of sulphuric acid on them? What colour do they give to the flame when tested on the platinum wire? What element is there in these crystals which exists in common salt? What part of the sulphuric acid united with what part of

* The full statement is "the formula of the molecule of the chlorides," but the form given in the text is very common. It should never be forgotten that the formula always stands for a certain definite amount of the substance, and shows that it is composed of the elements in certain definite proportions.

the common salt to form hydrochloric acid? Sulphuric acid, as you were told some time ago, contains hydrogen, sulphur, and oxygen, and it has been found that the formula H_2SO_4 represents the molecule. Usually when one element is removed from a compound another element takes its place. If sodium takes the place of hydrogen in sulphuric acid, it might be expected that two bodies could be formed, one whose formula would be $NaHSO_4$, and another whose formula would be Na_2SO_4. These two substances may be obtained by the action of sulphuric acid on common salt, and one of the arguments in favour of the formula H_2SO_4 for sulphuric acid is that these two compounds *can* be made. When they are produced by the action of sulphuric acid on salt, which of them will be obtained in a given case depends upon the relative quantities of salt and sulphuric acid used and the temperature to which the mixture is heated, the higher temperature giving the salt with the greater proportion of sodium.

Compounds obtained from sulphuric acid by replacing the hydrogen by metals are called *sulphates*. Ordinary salt is formed from hydrochloric acid by replacing the hydrogen of hydrochloric acid by sodium, as you saw in your experiment of heating sodium in a current of the gas. Since the sodium sulphates are produced by replacing the hydrogen of sulphuric acid by sodium they are also called salts. When the sodium of common salt replaces the hydrogen of sulphuric acid, the hydrogen at the same time replaces the sodium, uniting with chlorine to form hydrochloric acid. There is thus "*double decomposition*," two elements or groups of elements changing places. The salt derived from sulphuric acid by replac-

ing half of the hydrogen by sodium is sometimes known as sodium hydrogen sulphate, and the other salt disodium sulphate. Test the laboratory specimens of these two salts with litmus. You should find one neutral and the other acid. To a solution of the acid salt add caustic soda to see if you cannot make it neutral. Which contains the most sodium, the acid salt or the neutral salt? Is the sodium hydrogen sulphate the acid or the neutral salt? Which salt has a formula most nearly approaching that of sulphuric acid? The names acid sodium sulphate and neutral sodium sulphate are more frequently used than sodium hydrogen sulphate and disodium sulphate. Even the word "neutral" is often left out, and sodium sulphate means the neutral salt. Since the acid sulphate requires twice as much acid for its formation as the neutral salt does, it is sometimes called the bisulphate; so that you see there are occasionally a number of names for the same substance, each name laying emphasis on a different fact.

You have learned that sodium chloride acted on by sulphuric acid gives hydrochloric acid and sodium sulphate or sodium acid sulphate. Which of these requires the higher temperature for its production? The way in which the hydrogen and sodium change places is brought out better, if we call sulphuric acid hydrogen sulphate and hydrochloric acid hydrogen chloride, as the formulæ show we may readily do. We may say, sodium chloride and hydrogen sulphate yield hydrogen chloride and sodium sulphate. If at the proper temperature we start with a certain amount of sodium chloride and add just the right quantity of hydrogen sulphate, we shall obtain all of the sodium in the form of sulphate, and all of the hydrogen in the form of chloride. If we put in too much sulphuric

acid, we shall have some of it left over; if too little, we shall have some of the sodium chloride unchanged.

Equations. — It is usual for chemists to state these facts in a short way by using "*Equations.*" The formulæ of the substances entering into the reaction are written first and the sign + is put between them, then comes the sign of equality, and then the products of the reaction, thus:

$$\mathbf{NaCl} + H_2SO_4 = \mathit{HCl} + \mathbf{NaHSO_4}.^*$$

The formula NaCl stands for a certain definite amount of sodium chloride, the formula H_2SO_4 stands for a certain definite amount of sulphuric acid, and so with the formula of each of the other substances; and hence the equation not only expresses what substances are produced by the reaction of the other substances, but also how much of each is required or produced in the reaction. The symbol Na stands for 23 parts by weight of sodium, the symbol Cl stands for 35.5 parts by weight of chlorine. We do not know the weight of the atom of sodium nor of the atom of chlorine, but we know that the atom of sodium weighs 23 times as much as the atom of hydrogen, and that the atom of chlorine weighs 35.5 times as much as the atom of hydrogen. In a molecule of common salt, then, the weight of the sodium is 23 as compared with the weight of chlorine 35.5, and if we assume that larger quantities are made up of molecules, for every 23 ounces or pounds or grammes of sodium in a quantity of common salt, there must be 35.5 ounces or pounds or grammes of chlorine. It is evident that the quantity of common salt

* In the equations of this book the formulæ of solids are printed in black type, and of gases in italics. Plain type indicates that the substance is a liquid or in solution.

containing this quantity of sodium and chlorine must be 58.5 ounces or pounds or grammes. The atom of sulphur weighs 32 times as much as the atom of hydrogen, and the atom of oxygen 16 times as much as the atom of hydrogen, so that the formula H_2SO_4 represents the weight $2 + 32 + 64 = 98$, and our equation represents that 98 parts by weight of sulphuric acid are required for 58.5 parts by weight of common salt. Also 36.5 grammes of hydrochloric acid would be produced, and 120 grammes of sodium acid sulphate. These relationships of weight do not depend upon the atomic theory; they are matters of experiment and have to deal with the character of the substances, not upon any *theory* that we may hold regarding the ultimate structure of matter; but as during nearly a undred years the atomic theory has stood its ground and no facts have been learned to upset it, we often speak as though we were as sure of *it* as we are of the experimental results obtained by analysis.

It must be remembered that equations represent only the result of experiment; they form a short and convenient method of describing what takes place in a reaction, but what *does* take place can be learned only by experiment. It must also be remembered that the atomic weights that we use have been obtained by very careful experiment. Many chemists have devoted years to these experiments, and many more years will doubtless be expended in the same way in order to obtain still more accurate results.

You have learned enough of chemistry by this time to expect that the weight of the substances produced by a reaction must always be equal to the weight of the substances entering into the reaction, and you may always

know that an equation is wrong if the weight represented on one side of the equation is not exactly equal to the weight on the other side, or (making the statement in terms of atoms) if every atom represented on one side of the equation is not found on the other side of the equation. In the equation we have been considering, for example, it is represented that one atom of sodium, one of chlorine, one of sulphur, two of hydrogen, and four of oxygen enter into the reaction. These merely change their places, and in the products there are one atom of sodium, one of chlorine, one of sulphur, two of hydrogen, and four of oxygen. On the left hand side the two hydrogen atoms are together in the molecule of sulphuric acid; on the right hand side they are separated and in different molecules, but there are the two atoms in both cases.

The equation does not tell the conditions under which the experiment is carried out, and very frequently the course of the reaction depends upon the conditions. In this case, for instance, if a high temperature is used, the neutral sodium sulphate is produced, and the equation must represent that fact, if it is to be correct for these conditions.

The equation is

$$2\,\mathbf{NaCl} + H_2SO_4 = 2\,\mathit{HCl} + \mathbf{Na_2SO_4}.$$

The 2 in front of the formula NaCl means that two molecules of sodium chloride are represented as entering into the reaction, or that twice the quantity, 58.5 of sodium chloride, must be provided for 98 of sulphuric acid to act upon. It will be seen, then, that only half as much sulphuric acid, in proportion, is needed in this case as in the former, and so if hydrochloric acid is required, it

would appear cheaper to use a high temperature. We must always consider the circumstances, however, before drawing hasty conclusions. In this case the neutral sodium sulphate is liable to harden upon the glass, and is difficult to remove from the flask, while the acid sulphate does not present this difficulty. A flask broken in attempting to clean it would cost more than the extra sulphuric acid. On the large commercial scale, however, it is cheaper to use a high temperature and a smaller quantity of sulphuric acid, and besides, in the commercial process neutral sodium sulphate is required as much as hydrochloric acid is.

To calculate how much sulphuric acid is required to convert a given amount of sodium chloride into sulphate is easy. Suppose, for instance, we wish to know how much sulphuric acid is required for 100 grammes of sodium chloride. We know that for $2 \times 58.5 = 117$ grammes of sodium chloride 98 grammes of sulphuric acid are required; therefore, 100 grammes of sodium chloride will require

$$98 \times \frac{100}{117} = 83.76 \text{ grammes.}$$

In a similar way it could be calculated how much hydrochloric acid and how much sodium sulphate would be produced.

Statement regarding the Occurrence and Properties of Hydrochloric Acid. — Hydrochloric acid is to a certain extent given off from volcanoes, or from the lava which has recently flowed out from volcanoes, but the amount is comparatively small. The method of its preparation has been sufficiently discussed and so have most of its properties. Its density compared with air as unity is approximately 1.26. At the temperature of 10° C. it liquefies under a pressure of forty atmospheres. Liquid

hydrochloric acid is lighter than water and freezes at $-112.5°$ C. It is much more readily condensed than such gases as oxygen and hydrogen, and was one of the first gases to be compressed into the liquid form. The gas which is so readily condensed is also readily dissolved in water, and at 0° C. 500 volumes or more of the gas are dissolved by one volume of water. The strongest solution has a specific gravity 1.2. When the strongest hydrochloric acid solution is heated, it loses a greater proportion of gas than of water, becoming weaker and of lower specific gravity until it reaches a specific gravity 1.1. On the other hand, when a very dilute solution is heated, more water in proportion is given off, and the acid becomes stronger till it reaches the specific gravity 1.1. So whether a very strong or a very weak acid be evaporated, the solution ultimately obtained in the evaporating vessel will have the specific gravity 1.1, and boil at the temperature 110° C. These numbers can easily be remembered and are interesting. Any acid either stronger or weaker boils at a lower temperature than 110°, and the temperature will be the lower, the stronger the acid, if its specific gravity is more than 1.1; or the weaker the acid, if the specific gravity is less than 1.1. If there were just a very little gas dissolved, the boiling point of the solution would be very near to 100°, the boiling point of pure water. The acid of 1.1 specific gravity is often called the acid of constant boiling point.

Hydrochloric acid acts on zinc and iron, setting free hydrogen in just the same way as sulphuric acid does, the chloride of zinc and of iron being produced at the same time. The other chemical properties of hydrochloric acid have been pretty fully studied by you already.

CHAPTER X

THE HALOGENS

Laboratory Preparation of Chlorine, and Experiments with the Gas. — EXPERIMENT 43. Fit up an apparatus as for making hydrochloric acid, but into the flask put about 200 c.c. strong hydrochloric acid, and then about one-quarter of its weight of coarsely powdered manganese dioxide. Heat gently, never allowing the flask to become so hot that you cannot easily hold your hand on it. Why should you be careful not to heat strongly? When strong hydrochloric acid solution is heated, does it become stronger or weaker? What gas is produced in the flask?

A hood or the lime tower is even more necessary in these experiments than in the preparation of hydrochloric acid, and you must be very careful not to inhale the gas. If possible the operation should be conducted under a hood. Collect a number of bottles or cylinders of chlorine by downward displacement or over hot water. Does hot water or cold absorb gases the more readily? Why should hot water be used when chlorine is to be collected, while hydrogen is usually collected over cold water? Strong brine would serve the same purpose as hot water.

Is chlorine lighter or heavier than air? Lower a small bottle containing air into a larger one containing chlorine, and see whether you can dip out some of the chlorine.

Light a jet of hydrogen and introduce it into a jar of

chlorine as in Fig. 32. What change do you notice in the appearance of the hydrogen flame? What change in the colour of the gas in the jar? What is produced when hydrogen burns in chlorine?

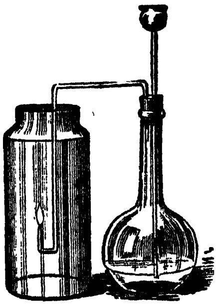


Fig. 32

Light a candle, and hold over the flame, just above the luminous part, a test-tube containing cold water but dry on the outside. What do you now see on the outside of the test-tube? What is thus shown to exist in the candle? What does this element take from the air in order to produce the substance on the test-tube? Would anything else have appeared on the test-tube if held in the luminous part of the flame? Now introduce the lighted candle into a cylinder of chlorine, being careful to lower it gradually. What proof have you that there is a part of the candle which burns in air but does not burn in chlorine? What part of the candle *does* burn in chlorine?

Warm a little turpentine in a test-tube, taking care that the turpentine does not catch fire. Dip a piece of filter-paper into the turpentine and bring it at once into a jar of chlorine. If your experiment is successful, the turpentine will catch fire. What is the peculiarity of the smoke?

What two elements exist in ammonia? Which of them would be the more likely to combine with chlorine? What would it form? What would be produced by this substance combining with more ammonia? Put a piece of paper moistened with strong ammonia water into chlorine, and see if your results are what you might expect. Has

the substance produced, as irritating an effect on the eyes and nose and throat as chlorine has? If there is a quantity of chlorine in the air of the laboratory, what would be a convenient substance to use in order to get rid of it? Will it make the air of the laboratory *look* more or less clear?

Into another cylinder of chlorine introduce a piece of phosphorus on a deflagrating spoon. Do not light the phosphorus before putting it into the chlorine. What evidence have you that the chlorine acts on the phosphorus? How does the behaviour of phosphorus in chlorine compare with that of phosphorus in oxygen?

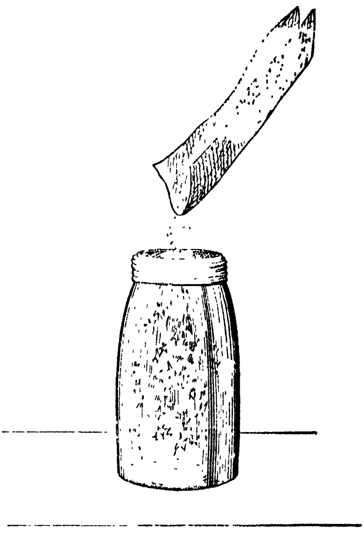


FIG. 33

As in Fig. 33, shake some finely powdered arsenic and finely powdered antimony into the chlorine contained in another jar. What do you observe? In all of these experiments be specially careful not to inhale the fumes, for they are not only irritating but very poisonous.

Heat a piece of sodium the size of a small pea or less in a deflagrating spoon, and so soon as it begins to burn, introduce it into chlorine, being careful that none of the sodium sputters into your face. Is the action more or less violent than when burn-

ing sodium is introduced into hydrochloric acid gas: When sodium is burning in hydrochloric acid it must separate the chlorine from the hydrogen. Is this done when sodium is burning in chlorine? What reason is there for the action being more violent in one case than in the other? What substance is produced when chlorine acts on sodium?

Chlorine Water.—Bleaching.—EXPERIMENT 44. Pass chlorine into water. What evidence have you that the water absorbs some of the chlorine? The solution of chlorine is usually called *chlorine water*. Pour some chlorine water into a little indigo solution, or into water containing ink. What happens to the colour? Write with ordinary ink on a piece of paper on which there is print. What difference is there in the action of chlorine water on the ink with which you have written and on the printer's ink? Put a piece of coloured cloth into chlorine water and see what happens. Chlorine is very much used for bleaching cloth, paper, and numbers of other things. It is not usually applied in the form of chlorine water, because other methods are more convenient on the large scale. A great many of the colouring matters are substances which become colourless when acted on by oxygen; and chlorine with water produces oxygen. This may be shown by allowing chlorine water to stand in the sunlight for several days, when the greenish colour of the water disappears, while oxygen and hydrochloric acid are formed. The action is represented by the equation

$$2\ H_2O + 2\ Cl_2 = 4\ HCl + O_2.$$

If some substance be present that combines readily with oxygen, the chlorine will be rapidly used up, the oxygen

not being set free, but combining with the other substance. The reaction will not require several days, but in all probability only a few seconds. The colouring matters bleached by chlorine are usually those that are made colourless by oxygen. Chlorine and water and the colouring matter produce hydrochloric acid and a colourless substance. Printer's ink is composed largely of lampblack, the soot from burning resin, and is not acted on by oxygen, hence is not bleached by chlorine water.

Chlorine is used as a disinfecting agent, destroying noxious odours and disease germs. The action is somewhat similar to that in bleaching; but in the case of disease germs chlorine probably acts in part simply by killing those lower forms of life in the same way as it would kill higher plants and animals. Small quantities of chlorine are found effective for the purification of drinking water, any excess of chlorine being removed by filtering through charcoal.

It will be advisable to study the process by which chlorine is produced from manganese dioxide, and to express the action in the form of an equation. What is the formula of manganese dioxide? How many chlorine atoms correspond to one oxygen atom; for instance, what is the formula of the chloride corresponding to the oxide CaO? What is the ordinary name for this oxide? What would be the formula of the chloride corresponding to manganese dioxide? This chloride, if formed at all, very readily decomposes, losing half of its chlorine, which escapes in the form of gas, and for this reason chlorine can be obtained by the method described. Why cannot we make chlorine by the action of hydrochloric acid on mercuric oxide?

How many atoms of hydrogen are necessary to combine with *two* atoms of oxygen? How many molecules of hydrochloric acid are necessary to supply that number of hydrogen atoms? Putting the facts you have learned into the form of an equation, we have

$$\underset{\text{Manganese dioxide}}{\mathbf{MnO_2}} + \underset{\text{Hydrochloric acid}}{4\,HCl} = \underset{\text{Manganese chloride}}{MnCl_2} + \underset{\text{Water}}{2\,H_2O} + \underset{\text{Chlorine}}{Cl_2}.$$

How much of the chlorine in hydrochloric acid is set free as gas? What becomes of the rest of it? The equation represents that $4 \times 36.5 = 146$ grammes of hydrochloric acid are required for 87 grammes of manganese dioxide. Why should the acid that you took weigh at least four or five times as much as the manganese dioxide, if you desired to use up all of the manganese dioxide? Would 36.5 grammes of the acid you took be represented by the formula HCl?

Number of Atoms in the Molecule of Hydrogen and of Chlorine. — In our equations we usually wish to represent molecules as taking part in the reaction. How many atoms are there in a molecule of hydrogen? How many in a molecule of chlorine? In order to represent the reaction which takes place when hydrogen burns in chlorine, which is the better form of equation,

$$H + Cl = HCl,$$

or

$$H_2 + Cl_2 = 2\,HCl?$$

It is found by experiment that one volume each of hydrogen and chlorine unite to form two volumes of hydrochloric acid. If Avogadro's law is true, that equal volumes of different gases contain the same number of molecules, could

H represent the molecule of hydrogen, and Cl the molecule of chlorine, HCl representing the molecule of hydrochloric acid? On this last assumption what volume of hydrogen would be represented by H, what volume by Cl, what volume by HCl?

What would the equation

$$H + Cl = HCl$$

represent in that case regarding the volumes of hydrogen, chlorine, and hydrochloric acid? Would that represent the facts of experiment?

What is the weight of chlorine as compared with hydrogen? If we use the symbol H to represent a gramme of hydrogen, what weight would be represented by H_2? What weight by Cl_2? *

Does a gas expand or contract if more pressure is put upon it? Does it expand or contract if its temperature is raised? Two grammes of hydrogen always occupy the same volume if the temperature and pressure are the same. It is usual to give the volume of a gas at the temperature of melting ice, 0° C., and the ordinary atmospheric pressure, which is the pressure that would be exerted by a column of mercury 760 millimetres high. Two grammes of hydrogen represented by the formula H_2 at the temperature 0° C. and the pressure 760 millimetres occupies the volume 22.412 litres. Also 71 grammes of chlorine represented by the formula Cl_2 occupies the volume 22.412 litres at 0° C. and 760 millimetres. This volume is called the gramme molecular volume, because it is the volume which the gas occupies if the symbols which represent the molecular weight are used to represent grammes. Hydrochloric acid is a gas whose molecular weight is represented

* See Appendix C.

by the formula HCl, and the weight 36.5 grammes occupies the volume 22.412 litres. What volume is represented by the formula 2 HCl?

What does the equation

$$H_2 + Cl_2 = 2\,HCl$$

represent regarding the volumes of the gases?

When water vapour is formed from hydrogen and oxygen, the equation representing the reaction is

$$H_2 + O = H_2O,$$

or
$$2\,H_2 + O_2 = 2\,H_2O.$$

Which is the better form of equation? Which represents the molecule of oxygen? What volume of water *vapour* is obtained from two volumes of hydrogen united to one volume of oxygen?

Ideas conveyed by a Chemical Formula. — A chemical formula should always represent one of three things:

First, a molecule of the substance as made up of a number of atoms, each having a certain definite weight which we do not know, though we know with a fair degree of accuracy the weight of one atom as compared with that of another. The molecular weight is the weight as compared with that of an atom of hydrogen.

Second, a weight of the substance in grammes, one gramme being made the unit of weight instead of the unknown weight of the atom of hydrogen. The formula then represents the gramme molecule.

Third, in the case of gases and of gases only, a certain definite volume called the gramme molecular volume, which is the volume of the gramme molecule of the gas at 0° C. and 760 millimetres pressure. There is no simple relation

between the volume and the weight of liquids and of solids, as there is of gases, and hence formulæ do not represent volume in these cases. We can tell from the formula of hydrochloric acid what the volume of a certain weight of the gas would be at 0° C. and 760 millimetres pressure, but we cannot tell from the formula what the volume of water or sand would be under the same conditions. Knowing that the formula of the molecule of oxygen is O_2, how many grammes of oxygen occupy the volume 22.412 litres? How many grammes of nitrogen occupy the same volume? Air is made up of these two elements for the most part, and the weight of air occupying the volume 22.412 litres is 28.88 grammes. If we know the molecular weight of a gas, we can therefore always tell whether it is lighter or heavier than air.

Bromine. — What is obtained when strong sulphuric acid acts on common salt? What is obtained when hydrochloric acid acts on manganese dioxide? You remember that you treated No. 1 of the series of salts in the last chapter, with manganese dioxide and sulphuric acid. What was the gas obtained in that case? What was the appearance of the vapour obtained from No. 2 by the same action? Was the metal in No. 2 the same as in No. 1, or was it different? What reason have you for supposing that the vapour obtained by the action of manganese dioxide and sulphuric acid was similar to, though not identical with, chlorine? The vapour was that of bromine, so named on account of its very disagreeable and irritating odour (from the Greek word *bromos*).

What is the chemical name of No. 1, which you found to consist of sodium and chlorine? What is the name of No. 2, which you now know to consist of sodium and

bromine? What is obtained by the action of sulphuric acid on sodium chloride? What might you expect to get by the action of sulphuric acid on sodium bromide? What evidence have you that if hydrobromic acid is obtained at all it is not the only thing obtained? What elements do you judge from the name hydrobromic acid to exist in that substance? What reason have you for supposing that they do not form so *stable* a compound (that is, a compound difficult to decompose) as hydrogen and chlorine? Would you expect hydrogen to burn in bromine as readily as in chlorine?

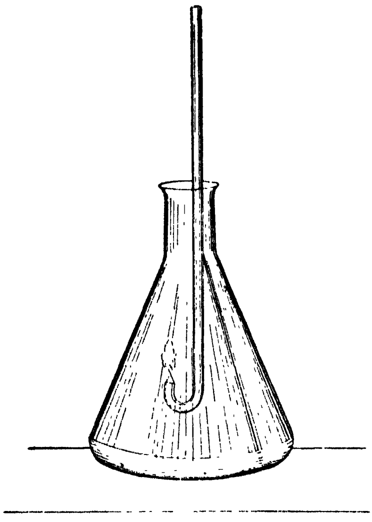


FIG. 34

EXPERIMENT 45. Try whether a jet of hydrogen will burn in bromine vapour. To do this put a few drops of liquid bromine into a wide-mouthed bottle, or into a flask shaped like that in the figure (Fig. 34). Such a flask is called an *Erlenmeyer* flask, and may be warmed without danger of breaking. Introduce a burning jet of hydrogen. What is the result? If you have no liquid bromine at hand, you can prepare some of the vapour from potassium bromide. Slowly add eleven volumes of strong sulphuric acid to eight volumes of water, and when the mixture is cool mix

with manganese dioxide. This may be done in the Erlenmeyer flask. Then add potassium bromide as required, and heat gently. Introduce a candle into the bromine vapour. Does it burn? If you have liquid bromine pour a few drops of it into turpentine. If not, pour some of the bromine vapour into turpentine and shake up so that the bromine may come into contact with the turpentine. What evidence have you that chemical action has taken place? What evidence have you that the action is not so violent as when chlorine acts on turpentine? Turpentine consists of carbon and hydrogen; when chlorine acts on it, the hydrogen is all removed and the carbon set free as a dense smoke. When bromine acts on it, a part only of the hydrogen is removed, and some bromine takes its place, giving a colourless compound. This process is called *substitution*. We say that bromine is substituted for part of the hydrogen, or that part of the hydrogen is *replaced* by bromine. The hydrogen removed combines with bromine, forming colourless hydrobromic acid. Half of the bromine that enters into the reaction replaces hydrogen, the other half combines with the hydrogen so replaced.

EXPERIMENT 46. Introduce into bromine vapour a piece of phosphorus in a deflagrating spoon, as in Fig. 35. What do you observe? Set fire to a piece of sodium, and put it into bromine vapour. What is produced?

EXPERIMENT 47. Put a few drops of bromine into about ten times as much water. What evidence have you that water dissolves bromine? Does bromine mix with water in all proportions as alcohol does? Which is the heavier of the two liquids? Add a few drops of bromine water to a larger quantity of water, and then add a little carbon

bisulphide (or disulphide).* What elements do you judge by the name, to exist in carbon bisulphide? Remembering the formula of carbon dioxide, what would you expect the formula of carbon disulphide to be? Is carbon bisulphide heavier or lighter than water? Does it dissolve bromine more or less readily than water? What is the colour of a solution of bromine in carbon bisulphide?

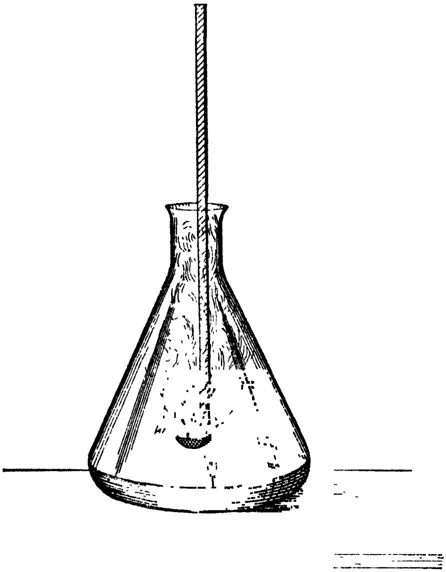


Fig. 35

To some water containing a little ink, or similar colouring matter, add bromine water slowly until you see some decided effect. What is the effect?

To a solution of potassium bromide add a few drops of chlorine water, and then a little carbon bisulphide. What is the colour of the carbon bisulphide, when the liquid is shaken up? To what is the colour due? If just enough chlorine water were added, and the bromine produced

* The name disulphide is not so good as bisulphide, for the prefix is Greek and the main part of the word is Latin.

were removed, what substance would be left in solution in the water?

Since, when chlorine is added to a metallic bromide, bromine is set free, chlorine is said to have a stronger affinity for a metal than bromine has. Did sodium burn more or less violently in bromine than in chlorine?

Iodine. — What happened when you treated No. 3 of the series of salts with manganese dioxide and sulphuric acid? Was the substance obtained either chlorine or bromine?

EXPERIMENT 48. Repeat the experiment, gently heating the lower part of the test-tube. Notice what collects in the upper part of the tube. Is it a solid or a liquid? What is its colour? What is the colour of the vapour before condensation? The substance is called iodine on account of this colour, the name being derived from a Greek word, as are most of the names in chemistry. What is the chemical name of No. 3?

EXPERIMENT 49. Add some iodine to turpentine. What evidence have you that it acts less energetically than bromine? What action is there? Put a small piece of phosphorus in a bottle or on a block of wood, and sprinkle a little iodine upon it. You should find that the union produces flame, so you must be careful.

EXPERIMENT 50. Try to dissolve iodine in water. Is it *readily* or *sparingly* soluble? What is the colour of the solution? Now add a little carbon bisulphide to the *aqueous* solution (the solution in water). Does iodine dissolve better in water, or in carbon bisulphide? To a solution containing a very little potassium iodide (a very small crystal in a good deal of water), add a few drops of bromine water and a little carbon bisulphide, and

then shake. Does the carbon bisulphide assume the colour due to bromine or to iodine? Which of these elements has the greater affinity for potassium?

EXPERIMENT 51. Grind up a few grains of starch with enough cold water to make a fluid of a creamy consistence, then add to about twenty times as much boiling water, and boil half a minute or so. Dissolve a very little potassium iodide in water and add a few drops of the starch paste just made. What is the colour? Then add a drop or two of chlorine water. What change is there in the appearance of the starch? Divide the liquid into two parts. Heat one. What happens to the colour? Allow to cool and notice the colour again. To the second portion add a little caustic potash or soda. What about the colour? What is the effect of allowing to stand in this case?

Statement regarding the Occurrence, Preparation, and Properties of Chlorine, Bromine, and Iodine. — You have now learned a good deal about chlorine, bromine, and iodine. You naturally do not expect them to be found free in nature because they so readily act on other substances. Sea-water, as every one knows, contains common salt more than half of whose weight is chlorine. It also contains bromides, but the bromine is less than $\frac{1}{300}$ part of the chlorine. It also contains iodides, but in exceedingly small quantity.

When a salt crystallises from a solution the liquid left behind is called the *mother liquor*. The mother liquor obtained from sea-water by evaporating till the common salt has separated out has a bitter taste on account of the magnesium salts in it, and is called bittern. It contains most of the bromine, which can be extracted either

by heating with manganese dioxide and sulphuric acid, or by chlorine. Most of the bromine of commerce is not obtained from sea-water, however, but from certain salt springs, which contain a larger proportion of the element. Almost all of the bromine used in America (over half a million pounds a year) is obtained from brines found in Michigan, Ohio and Pennsylvania, and West Virginia. Bromine or its compounds are used for making dyes, also in medicine and in photography.

Sea-water contains only a trace of iodine; but some sea-weeds (one or two kinds in particular) have the power of extracting iodine, which promotes their growth. From kelp, the ashes of these seaweeds, iodine was for a long time obtained, and is still to a certain extent prepared. The iodine in the ash is not far from 1% of the total weight. Iodine is now largely obtained from Chili, existing in small quantity in crude Chili saltpetre, which is mainly sodium nitrate. So much nitrate is required in commerce that though the amount of iodine in the crude salt is comparatively small, there is more than enough to supply the demand. Iodine and its compounds are used in medicine and in the manufacture of some dyes.

The similarity between the methods of obtaining chlorine from common salt, bromine from bittern, and iodine from the iodide in kelp, is shown by the equations

$$2\,NaCl + 3\,H_2SO_4 + MnO_2 = 2\,NaHSO_4 + MnSO_4 + 2\,H_2O + Cl_2$$
$$MgBr_2 + 2\,H_2SO_4 + MnO_2 = MgSO_4 + MnSO_4 + 2\,H_2O + Br_2$$
$$2\,NaI + 3\,H_2SO_4 + MnO_2 = 2\,NaHSO_4 + MnSO_4 + 2\,H_2O + I_2$$

The difference between the second equation and the others in the amount of sulphuric acid used is due to

magnesism not forming an acid sulphate similar to sodium hydrogen sulphate.

Chlorine is not only the most important of the three elements, but it was the first to be discovered, having been prepared by the Swedish chemist Scheele in 1774, while iodine was discovered in 1812 by Courtois, a Frenchman, and bromine in 1826 by Balard, also a French chemist. Bromine, in its character, is between chlorine and iodine, and was really obtained by Liebig several years before Balard's discovery, but Liebig, thinking that he was dealing with a compound of chlorine and iodine, did not test the substance, thus losing the credit of finding a new element. Chlorine is a gas, bromine a liquid, nearly three times as heavy as water, and iodine a solid, nearly five times as dense as water. Both bromine and iodine may be vapourised by heat; bromine, even at ordinary temperature, giving off considerable vapour. Iodine melts on being sufficiently heated, and the liquid boils. But long before the solid melts it gives off vapours. A substance that gives off vapour without melting is said to *sublime*. Many substances sublime to a slight extent, ice, for instance, which loses weight, even on a cold day when it does not melt; but iodine shows the property of subliming in a much greater degree.

Of the three elements we are considering, chlorine is the lightest in colour, while iodine is the darkest; chlorine is the most ready to combine with nearly all of the elements, iodine the least ready. Not only is there this gradation in properties, but there is a corresponding gradation in atomic weight. Chlorine has an atomic weight 35.5; 35.5 grammes of chlorine unite with one gramme of hydrogen to form 36.5 grammes of hydro-

chloric acid, represented by the formula HCl. The atomic weight of bromine is 80; 80 grammes of bromine are united to one gramme of hydrogen in 81 grammes of hydrobromic acid, represented by the formula HBr. Iodine has an atomic weight 127; 127 grammes of iodine are united to one gramme of hydrogen in 128 grammes of hydriodic acid, represented by the formula HI. How does the weight of all of these gases compare with air? What was your experience regarding the weight of chlorine, bromine vapour, and iodine vapour as compared with air?

Hydrobromic acid and hydriodic acid you have not prepared, because they are not important, and are not so easily prepared as hydrochloric acid. You remember they are not obtained in the same way. The properties of the three acids are as similar as those of the three salts, sodium chloride, bromide, and iodide. You have seen that the formulæ of the chlorides, bromides, and iodides are exactly similar, which shows that the valency of the three elements is the same in these salts. What *is* their valency in these compounds? The three elements unite directly with metals to form salts analogous to common salt, and are, therefore, called *halogens*, the word meaning "salt-formers."

Oxygen Compounds of the Halogens. — Neither chlorine, bromine, nor iodine has any great affinity for oxygen. Iodine is the only one that forms even moderately stable compounds, and these are decomposed by heat. There are compounds that contain hydrogen and oxygen, together with the halogen, but these compounds are not very important. The compounds containing halogen and oxygen together with a metal are more important. Of these, by far the most important are the *hypochlorites* and

the chlorates. These may be produced together with chlorides by the action of chlorine on such substances as caustic potash in solution. When chlorine acts on caustic potash the action may give potassium chloride and hypochlorite, or chloride and chlorate, according to circumstances.

The action is represented by the equations

$$2\,KOH + Cl_2 = KCl + \underset{\substack{\text{potassium}\\ \text{hypochlorite}}}{KClO} + H_2O$$

$$6\,KOH + 3\,Cl_2 = 5\,KCl + \underset{\substack{\text{potassium}\\ \text{chlorate}}}{KClO_3} + 3\,H_2O$$

Potassium hypochlorite readily gives up its oxygen, and is, therefore, a bleaching agent. The compound "bleaching powder" obtained by the action of chlorine on lime is much more commonly used. It resembles potassium hypochlorite in many respects. It is often called chloride of lime. It is used instead of chlorine water because more readily transported and more convenient to work with, but the principle of its action is the same, and, in fact, chlorine is produced from it in the process of bleaching. The chloride of lime is dissolved in water, the fabric is dipped into it and afterwards into dilute acid, and the chlorine produced causes the bleaching.

The most important chlorate is potassium chlorate, of which you have already had some experience. What is obtained by heating potassium chlorate?

The equation representing the reaction is

$$2\,KClO_3 = 2\,KCl + 3\,O_2.$$

What volume is represented by $3O_2$? How many

grammes of potassium chlorate are required to produce that volume of oxygen?

If potassium chlorate is mixed with a substance ready to combine with oxygen, the potassium chlorate is still more readily decomposed than when heated alone. A mixture of potassium chlorate and sugar explodes if placed on an anvil and struck by a hammer. A mixture of potassium chlorate and sulphur gives rise to explosions if rubbed by a pestle in a mortar. A *mortar* is a heavy bowl-shaped dish often made of porcelain, in which substances may be ground; the *pestle* is the instrument with which they are ground. These experiments are probably too dangerous for you to try.

When potassium chlorate has strong sulphuric acid put upon it, a greenish yellow gas, called chlorine peroxide, whose formula is ClO_2, is produced. It very readily decomposes with explosion, and the experiment is a dangerous one. The following experiment may, however, be performed with safety:

EXPERIMENT 52. Grind some potassium chlorate in a mortar till a fine powder is produced. Then grind separately about an equal quantity of white sugar, and mix the two by putting them upon paper and stirring them together. Do not think of mixing them in the mortar, as they might explode with the friction. Place the mixture in a long heap, say twenty times as long as it is wide. Dip a glass rod into sulphuric acid or take out a drop in a glass tube and touch one end of the heap with the acid. You should find that the mixture takes fire and burns from one end to the other, so be careful. The first so-called "chemical matches," which were invented about 1812, were not like our modern matches, but the head was

made of a mixture of potassium chlorate and sugar, and they were lighted by being dipped into sulphuric acid.

Fluorine is an element in many respects similar to chlorine, bromine, and iodine. It is still more active and hence very difficult to separate from its compounds, for as soon as separated from one substance it is ready to attack something else. Platinum is almost the only substance not attacked, with the exception of compounds such as fluorspar, which already have their full amount of fluorine.

CHAPTER XI

NITRIC ACID AND THE OXIDES OF NITROGEN

Nitric Acid. — EXPERIMENT 53. Taste some saltpetre. Does it most resemble an acid, an alkali, or a salt? What does it show with litmus?

How did you test for the metal in sodium chloride and potassium chloride? What colour is given to the flame by saltpetre? What is the metal?

Preparation of Nitric Acid. — Pour some strong sulphuric acid upon a little powdered saltpetre in a test-tube. What evidence have you that an acid is produced by the action? The acid is nitric acid. The salts of *nitric* acid are *nitrates*. As a general rule when the name of an acid ends in *-ic* the name of the salt ends in *-ate*. Nitrates may be considered as derived from nitric acid by replacing the hydrogen of nitric acid by a metal; or nitric acid may be obtained from a nitrate by replacing the metal by hydrogen.

This action is similar to that by which hydrochloric acid is obtained from a chloride. Just as the action of sulphuric acid on potassium chloride may be represented by the equation

$$\underset{\text{potassium chloride}}{\mathbf{KCl}} + H_2SO_4 = \mathbf{KHSO_4} + \underset{\text{hydrochloric acid}}{HCl.}$$

So the action of sulphuric acid on potassium nitrate may be represented by the equation

$$\underset{\text{potassium nitrate}}{\mathbf{KNO_3}} + H_2SO_4 = \mathbf{KHSO_4} + \underset{\text{nitric acid}}{HNO_3}.$$

It is not usual to speak of potassium *hydrochlorate* as the salt derived from *hydrochloric* acid in the same way as potassium *nitrate* is spoken of as the salt derived from *nitric* acid, because the name potassium chloride is simpler.

Compare the two formulæ, KCl and KNO_3. What group of atoms in the latter salt corresponds to the chlorine atom in the former?

A group of atoms which acts like a single atom in this manner is called a *compound radical.* That part of a salt which is not metal is called a *salt radical.* A salt radical may consist of a single element, or it may consist of a group of elements.

The formula HNO_3 represents that nitric acid contains oxygen. This formula is of course a result of experiment. The atomic weight of hydrogen being unity, of nitrogen 14, of oxygen 16, what proportion is the weight of oxygen of the total weight? Has nitrogen, as a general rule, a very great affinity for other substances? Has oxygen? What might you expect to happen if a substance which unites readily with oxygen be treated with nitric acid?

Experiments with Nitric Acid. — EXPERIMENT 54. Heat a little powdered charcoal in a deflagrating spoon till it begins to glow, and allow a drop or two of the strongest nitric acid to fall upon it, being careful that the acid does not spurt upon you. You should not pour the acid from a bottle, but take a very little in a glass tube so that you

will be sure not to have too much acid. The figure (Fig. 36) shows the method.

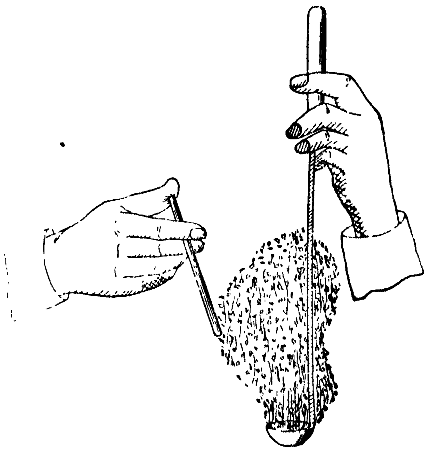


FIG. 36

EXPERIMENT 55. Pour into a porcelain evaporating dish enough of the strongest nitric acid to cover the bottom (certainly not more than $\frac{1}{8}$ inch deep; probably $\frac{1}{16}$ inch would be better). Place in the acid a small piece of phosphorus and then stand quite a distance away. The phosphorus should take fire and burn very vigorously, as shown in Fig. 37, and will probably be spattered about. The experiment should be performed under a hood, from which the fumes are carried away by a strong draught and which prevents the phosphorus flying widely about. If the acid form too deep a layer on the bottom of the porcelain dish, the phosphorus will not heat it so

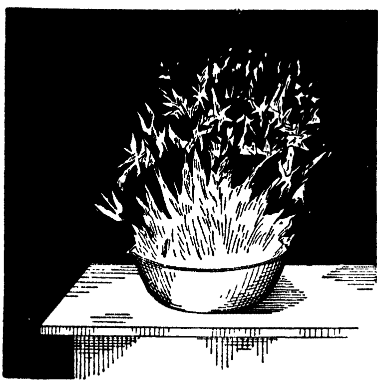


FIG. 37

readily, and will not take fire so soon. Reddish brown fumes come off, as well as the heavier white fumes of the burning phosphorus. The character of these red fumes you will learn later. As the burns produced by phosphorus are very severe, too much care cannot be taken.

What do you obtain when you neutralise caustic soda with hydrochloric acid?

EXPERIMENT 56. Into a porcelain evaporating dish, put some caustic potash solution and add enough nitric acid to make the solution slightly acid, then evaporate to dryness. Taste the solid produced. What is it? What chemical tests could you apply to find out whether you are correct in your judgment? What way have you already used to test for the metal and the acid in a salt?

Compare the two equations

$$NaOH + HCl = NaCl + H_2O$$

and

$$KOH + HNO_3 = KNO_3 + H_2O.$$

State in words the facts that these equations give in symbols. Of course there is water present with the alkalis and acids, though this fact is not represented in the equation. The equation does tell, however, whether there is more water before the acid and alkali are mixed or afterwards. Which is the case?

Not only does nitric acid give up oxygen to substances readily oxidisable, but so also does potassium nitrate when sufficiently heated.

EXPERIMENT 57. Heat some potassium nitrate in a test-tube, and test the gas produced, with a glowing splinter. What is the action of the gas on the splinter? Is the gas coloured or colourless? Bear this result in mind in order to compare it with that obtained in a later experiment.

Now, keeping the mouth of the test-tube turned from you, into the fused (or melted) nitrate, drop a little piece of glowing charcoal; the burnt end of a match will do. What do you see? In the same way introduce a little sulphur, either a small lump or some powder. What is there in the nitrate which makes the combustion so energetic?

It will now be interesting to try the action of nitric acid on several substances, and to make comparisons with the action of some other acids.

EXPERIMENT 58. Pour some strong hydrochloric acid upon a little cupric oxide. What evidence have you that action takes place when the acid is put upon the oxide? Is there a gas given off? What is the colour of the liquid? If you cannot see the colour of the liquid on account of the b ck solid mixed with it, you should separate the two. How can you do this?

Treat some cupric oxide in the same way with nitric acid, and make similar observations. How do the colours of the solutions compare? Now dilute the cupric chloride solution with water, and compare again. Dilute the cupric nitrate solution, and compare once more. Does the cupric chloride or the cupric nitrate change the more on dilution? The action in the two cases is represented by the equations

$$\mathrm{CuO} + 2\,\mathrm{HCl} = \mathrm{CuCl_2} + \mathrm{H_2O}$$

and
$$\mathrm{CuO} + 2\,\mathrm{HNO_3} = \mathrm{Cu(NO_3)_2} + \mathrm{H_2O}.$$

Judging by the formulæ given in the equations, is copper in these compounds a univalent or a bivalent element? Is the compound radical, NO_3, univalent or bivalent?

What becomes of the hydrogen in the two acids? What gas is given off when hydrochloric acid acts on zinc? If

you do not remember, try the experiment. What happens when hydrochloric acid is put upon copper? Would the equation written above for the action on the oxide need to be changed merely by leaving out the symbol for oxygen on each side of the equation?

Now try the action of nitric acid on copper. Would the equation written above for the action of nitric acid on cupric oxide need to be changed merely by leaving out the symbol for oxygen on each side of the equation? If so, what would be the colour of the gas produced? What *is* the colour of the gas that you see produced?

Try the action of nitric acid upon zinc, using dilute acid containing about ten times as much water as of strong acid.

Does it give the same gas as is given by copper? What is there in nitric acid for which hydrogen has a great affinity? Why should you think it likely that hydrogen would not be produced by the action of nitric acid on a metal?

EXPERIMENT 59. Pour the strongest nitric acid upon some granulated tin. After a minute or so add about an equal quantity of water to the acid. Does weak or strong nitric acid act most energetically upon tin? Mix some of the white paste produced in this reaction with lime. What smell is obtained? Assuming that you had not been told of the composition of nitric acid, how would this experiment prove that the acid contains nitrogen? Would it also prove that hydrogen exists in nitric acid? Give reason for your answer.

Pour dilute nitric acid upon some bright pieces of iron wire in a test-tube. Notice the effect. Upon some similar pieces of wire, pour the strongest nitric acid. How does

the action compare in the two cases? Now add water to the strong acid. How does the action now compare with that observed when the weak acid was poured directly upon the iron in the first case? Last of all, with a copper wire, touch (for a moment merely) the iron wire that is not acted on, and remove the copper wire at once from the liquid. What do you observe? The iron when unacted upon in the above instance is said to be in the passive state. The cause of the "passive state" is not known. though there has been a great deal of speculation about it.

Statement regarding the Occurrence, Preparation, and Properties of Nitric Acid. — Nitric acid is produced to a slight extent by the electric discharge during thunder storms, but is practically obtained from nitrates. The ultimate result of the decay of organic matter, in so far as the nitrogen is concerned, is the formation of nitrates. An intermediate step is the formation of ammonia. These changes are brought about by different kinds of bacteria. The presence of nitrates in water points to contamination with sewage; but as the nitrogen in the sewage requires time for its conversion into nitrate, the harmful parts of the sewage have probably been destroyed by the time that nitrates are found. But as this is not certain to be the case, water containing much nitrate is suspected, though the presence of ammonia is much more serious.

In most cases, the nitrates produced in the soil are not allowed to accumulate, being washed out by water or used up by growing plants; but in dry countries, nitrates are found as a crust on the surface of the soil, particularly in the neighbourhood of towns. Potassium nitrate, called nitre or saltpetre, is largely found in India and Egypt in this way. In Chili there are enormous beds of sodium

nitrate known as Chili saltpetre. In this country calcium nitrate is found in some dry caves.

Nitric acid is produced on the large scale from potassium nitrate or sodium nitrate. The following equations represent the reaction by which the nitric acid is obtained:

$$KNO_3 + H_2SO_4 = KHSO_4 + HNO_3$$
$$NaNO_3 + H_2SO_4 = NaHSO_4 + HNO_3$$

Would the weight of sodium nitrate required to produce a certain quantity of nitric acid be more or less than the weight of potassium nitrate? A comparison of the two equations just given should enable you to answer this question. Sodium nitrate is more difficult to purify than potassium nitrate, and therefore the latter was for a long time used in making nitric acid, but now most of the acid prepared commercially is obtained from sodium nitrate.

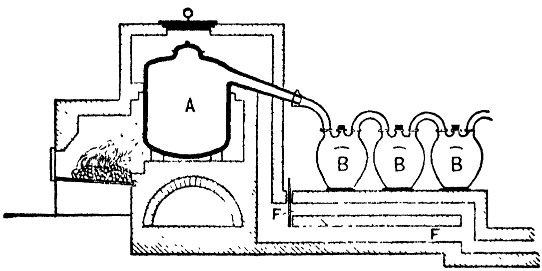


FIG. 38

The sodium nitrate is heated in large retorts made of cast iron, and the nitric acid is condensed in glass or earthenware jars as in Fig. 38. What objection would there be to attempting to make dilute nitric acid in iron retorts, by using nitrate and dilute sulphuric acid? Why does

the same objection not hold against producing strong nitric acid in this way, with the nitrate and strong sulphuric acid? The strongest nitric acid has a density of about 1.5. If it is boiled it becomes weaker, till finally an acid which contains 68% of the pure acid, the remainder being water, is left behind. This acid has a constant boiling point 123° C. and a specific gravity 1.42. This constant composition and boiling point exist at atmospheric pressure, but vary when distillation is made at other pressures. A similar statement may also be made about hydrochloric acid of constant boiling point.

The formula for nitric acid is HNO_3. One molecule alone does not afford enough hydrogen to produce a molecule of water, but two molecules contain sufficient hydrogen for the purpose. Phosphorus pentoxide, which you obtained by burning phosphorus in oxygen or in air, is very ready to take up water from substances which contain oxygen and hydrogen. Phosphorus pentoxide takes away water from two molecules of nitric acid, and the other parts of these two molecules unite to form one molecule of nitrogen pentoxide, or nitric anhydride. The name *anhydride* is given to an oxide which will unite with water to form an acid. In this case *phosphoric anhydride* takes water from nitric acid and becomes *phosphoric acid*, and owing to the loss of water the nitric acid is changed into nitric anhydride.

In order to represent nitric acid as made up of water and nitric anhydride, the formula may be written H_2O, N_2O_5, which is, for the purpose, a convenient form (though it does not represent the molecule as a formula usually does). When the comma is written between the H_2O and the N_2O_5, it represents that the compound nitric acid

is meant,—not that the water and nitric anhydride are separated.

The equation

$$H_2O,\ N_2O_5 = H_2O + \underset{\substack{\text{nitric}\\ \text{anhydride}}}{N_2O_5}$$

indicates that the compound is decomposed in some way, and that the water is separated from the anhydride.

Nitric anhydride is a white crystalline solid, which readily unites with water to form nitric acid. It is very liable to decompose into oxygen and an oxide of nitrogen containing less oxygen than nitric anhydride. It is not important practically, and is introduced here mainly on account of its chemical relationships.

Oxides of Nitrogen derived from Nitric Acid.—Let us consider more fully the formula $H_2O,\ N_2O_5$. You have seen that it is possible to remove the water from two molecules of nitric acid, thus obtaining the body nitric anhydride with the formula N_2O_5; and that this substance is ready to decompose into oxygen and a lower oxide of nitrogen (that is, an oxide containing less oxygen than nitric anhydride). It is conceivable that by removing water and oxygen from nitric acid the following bodies might be obtained:

$$N_2O_4, \quad N_2O_3, \quad N_2O_2, \quad N_2O, \text{ and } N_2.$$

But it does not follow that because the formulæ can be *written* the substances can be *prepared*. As a matter of fact, however, they can be so prepared, with the possible exception of N_2O_3, though they are not usually obtained perfectly pure. What did you see when nitric acid acted upon tin? The vapour given off was mainly a substance

whose percentage composition corresponds to the formula N_2O_4. What weight of the gas would go into 22.412 litres if the formula is N_2O_4? What weight would go into 22.412 litres if the formula is NO_2? At a low temperature, *e.g.* 20° C., the vapour density corresponds to the formula N_2O_4; above 150° C. the density corresponds to the formula NO_2; so that it is evident that, on heating, one molecule breaks up into two,

$$N_2O_4 = 2\,NO_2.$$

Some change visibly takes place in the gas, for the colour, which is light-brown at low temperature, becomes almost black at high temperature.

It has been usually stated, that from nitric acid by its action on arsenic trioxide the compound N_2O_3 is obtained, but some doubt has lately been expressed by investigators in the matter, that such is the case.

Copper produces mainly the compound whose percentage composition would be represented by the formula N_2O_2, while the action of zinc produces some of the compound N_2O.* Nitrogen is obtained to a small extent in nearly all the reactions mentioned above. The substances have been spoken of by symbols instead of by names, since the symbols readily show the relationship to nitric acid, but it is now necessary to learn the chemical names. These compounds of nitrogen and oxygen give a very instructive illustration of how chemical names are formed.

* If the nitric acid have a strength of 1 : 10 approximately, a considerable amount of the compound N_2O is obtained, whereas if the strength be 1 : 4, very strongly coloured fumes are seen, doubtless due to the formation of the compound with formula NO, which unites with the oxygen of the air.

You have learned that the compound N_2O_5 is called nitric anhydride, because when combined with water it gives nitric acid. The compound N_2O_3 when combined with water probably gives nitrous acid, though the compound decomposes very rapidly. It is therefore called nitrous anhydride. There are still left the compounds N_2O, N_2O_2, and N_2O_4. N_2O_2 is called nitric oxide, N_2O is called nitrous oxide, and N_2O_4 nitrogen peroxide.

You have noticed that in the naming of the five compounds the word *nitric* occurs twice, and the word *nitrous* twice. It is important to see how the terminations *-ic* and *-ous* are applied.

Of the two compounds N_2O and N_2O_2, which has the more nitrogen in proportion? The suffix *-ous* is similar to the suffix *-ose* and means "full of." For example, verbose means full of words, lachrymose means tearful, or full of tears, vigorous means full of vigour or strength. So nitrous means full of nitrogen, and nitrous oxide has more nitrogen than nitric oxide. In the same way, nitrous anhydride contains more nitrogen in proportion to oxygen than nitric anhydride.*

There are two chlorides of mercury having the formulæ $HgCl$ and $HgCl_2$. Which is the mercuric chloride, which the mercurous? So there are two nitrates. What would be the formula of mercurous nitrate? What the formula of mercuric nitrate?

The name peroxide you have already met, as in the case of hydrogen peroxide. The prefix "per" is a contraction

* It is *usually* stated that nitric oxide is the oxide having more *oxygen*, and nitrous oxide the one having less oxygen. This is merely another way of expressing the same thing, but it does not take into consideration the meaning of the suffixes.

for "super" or "hyper," and a peroxide contains a large amount of oxygen.

Other names are given to the oxides of nitrogen, formed from the Greek numerals for one, two, three, etc.

The following list arranges the formulæ and names:

N_2O	Nitrous oxide	or	Nitrogen monoxide.
N_2O_2 or NO	Nitric oxide	"	Nitrogen dioxide.
N_2O_3	Nitrous anhydride	"	Nitrogen trioxide.
N_2O_4	Nitrogen peroxide	"	Nitrogen tetroxide.
N_2O_5	Nitric anhydride	"	Nitrogen pentoxide.

Not only can oxygen be taken from nitric acid, but hydrogen can be added, ammonia being produced; and in some of the experiments by which the oxides of nitrogen are prepared, ammonia is produced at the same time.

By far the most important oxides of nitrogen are nitrous and nitric oxide.

Nitrous Oxide. — EXPERIMENT 60. Put about ten or fifteen grammes of ammonium nitrate into a small flask and fit up as in Fig. 39.

Heat the solid till it melts, moving the flame about under the flask so that the heating will be uniform and not too great in one place.* When the liquid begins to boil, heat very carefully, removing the flame if necessary from time to time. The temperature should never be higher than just sufficient to give off the gas at a reasonable rate. What evidence is there that a little of the ammonium nitrate sublimes unchanged, or that if it breaks up into two parts, these recombine to form the original

* While holding the flame, tip the burner so that the hand will not be beneath the flask in case there should be an explosion. An explosion is not liable to happen, but it is best to be on one's guard.

substance? What is the name given to the form of decomposition by heat which is followed by recombination on cooling? Notice the evidence that water is produced when ammonium nitrate is heated. Collect several cylinders of the gas which escapes. This is nitrous oxide.

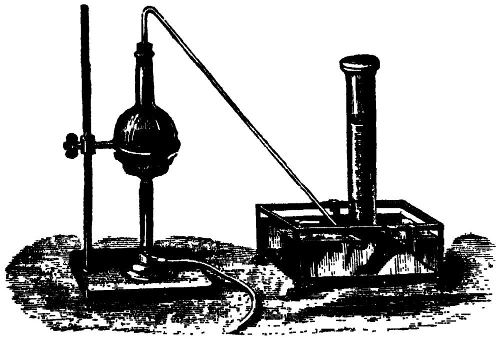


FIG. 39

The ammonium nitrate, as you saw, gives water and nitrous oxide. The reaction may be represented by the equation

$$NH_4NO_3 = 2\,H_2O + N_2O.$$

Assuming the formula N_2O as correct for nitrous oxide, what would be the weight of 22.412 litres? In this case would the gas be lighter or heavier than air? What experiments can you try in order to discover which is really the case? Try enough of these experiments to satisfy yourself as to the fact.

EXPERIMENT 61. Shake up a jar filled half with water and half with nitrous oxide, covering the mouth of the jar tightly with your hand. What evidence have you that nitrous oxide is soluble in water? What evidence have

you that it is not so soluble as ammonia or hydrochloric acid?

Introduce into a jar of nitrous oxide a glowing splinter of wood. What happens? Into another jar introduce in a deflagrating spoon a little burning sulphur just as soon as it is lighted and before it has begun to burn vigorously. Does it continue to burn or does it go out? Allow it to burn vigorously in the air and then introduce it into the gas. Is there any difference now in its behaviour?

Introduce into a cylinder of the gas some sodium in a deflagrating spoon. Does any change take place in the sodium? Now take it out and heat until it begins to burn, and again introduce it. How does the action compare in the two cases?

Try also what happens when burning phosphorus is introduced into nitrous oxide.

If you have any jars in which you can seal up the gas so that it may be kept for several days, preserve a jar full of the gas for future use.

Nitrous oxide is a gas with a sweetish taste. When inhaled it first produces a peculiar kind of intoxication which frequently shows itself in laughter, and hence the gas is called "laughing gas." The inhaling of a larger quantity produces insensibility to pain, and nitrous oxide is frequently employed by dentists for that purpose. It is more suitable than chloroform for minor operations, because the effects are not lasting. The gas as usually made, however, is liable to contain injurious impurities, and from these it must be purified.

Nitrous oxide is soluble in water to a considerable extent, and it is one of the gases more easily liquefied, requiring about thirty-one atmospheres pressure at 15°C. and

becoming liquid under atmospheric pressure at $-92°C$. It is supplied in liquid form in iron cylinders for the use of dentists and others.

Nitrous oxide supports combustion nearly as well as oxygen. How could the two gases be distinguished? To answer this question think of all the properties you know in which the gases are different.

When ammonium nitrate is heated too strongly, it decomposes partially in the manner represented by the equation

$$2\,\mathbf{NH_4NO_3} = 4\,H_2O + 2\,\mathit{NO} + \mathit{N_2}.$$

In this reaction, as well as in that represented by the previous equation, all the products except water are gaseous. How would the volumes of the gases compare in the two cases? What would be the comparative weight of the gaseous products? Why were you warned not to heat ammonia nitrate to a higher temperature than was necessary just to evolve a gas?

There are various ways in which it can be proved that the nitrogen and oxygen are combined in the proportions indicated by the formula N_2O. One method is to place some potassium in a tube filled with the gas over mercury, as shown in the figure (Fig. 40), and to apply heat till the potassium burns. After cooling, the gas left behind is found to occupy the same space as the nitrous oxide did, and to consist of nitrogen. But it is known that the weight of a given volume of nitrous oxide is to that of the same

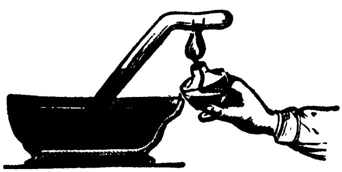


Fig. 40

volume of nitrogen as 44 : 28, therefore the weight of oxygen united to the nitrogen must have been 16; and the weight of the nitrogen is 28; hence the formula of the oxide must be N_2O.

Nitric Oxide. — EXPERIMENT 62. Fit up a flask or bottle, holding half a litre or less, with thistle-tube and delivery-tube for a gas, as in Fig. 41. Have all of your jars or cylinders ready for collecting the gas, because it should be collected quickly. Into the flask put a quantity of copper filings, then add water till the flask is about one quarter full, and then about an equal volume of strong nitric acid.

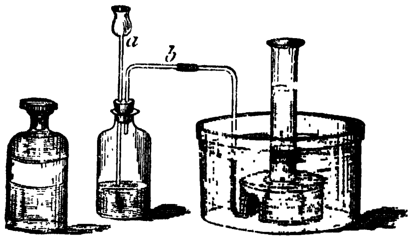


FIG. 41

Collect the gas as it escapes, keeping the first bottle separate from the others. Notice the colour that appears in the generating flask. How about the colour after the gas has been given off for a little while? What evidence have you that the colour of the gas that you first see is not that of the gas produced by the action of nitric acid on copper? If you do not *now* understand why there should be a difference between what you see at first and what you see afterwards, keep the *fact* in mind and try to discover some reason as you experiment further with the gas. Leaving aside the first cylinder or bottle of gas collected, test the solubility of nitric oxide by shaking up with water in the same way as you did in the case of nitrous oxide. Which is the more soluble of the two gases? Try whether a taper will burn in the gas.

Into another cylinder put some sulphur which is burning vigorously. How does the result compare with that obtained with nitrous oxide? Light a small piece of phosphorus and immediately (before it begins to burn vigorously) introduce it into a jar of nitric oxide. Does it continue to burn or does it go out? Introduce a piece of phosphorus which is burning vigorously. What happens this time? Which supports the combustion the more readily, nitrous or nitric oxide? Is it the oxygen or the nitrogen of these compounds which supports combustion? Which has the more oxygen, nitrous or nitric oxide? Which has the greater proportion of oxygen, nitrous oxide or water? Which will best support the combustion of a piece of wood? Which will best support the combustion of a piece of sodium? Water does not support the combustion of ordinary substances because the oxygen is so firmly attached to the hydrogen that only a few substances can take it away, but sodium is one of these substances, and the combustion of sodium is very vigorous. In nitric oxide nitrogen and oxygen are more firmly united than in nitrous oxide, and it is more difficult to separate them, but when they can be separated, as by burning phosphorus, the combustion is very vivid. Pour a few drops of carbon bisulphide* into a jar of nitric oxide, shake up so that the vapour of the carbon bisulphide may mix with the gas, and apply a light. What is the character of the flame? What part of the carbon bisulphide, if any, is left on the sides of the jar?

It has been already stated that the formula N_2O_2 represents the percentage composition of the gas, but it does

*** Carbon bisulphide is very inflammable, and care must be taken not to place the bottle near a flame.**

not necessarily follow that this is the proper molecular formula. If the proper formula is NO, how many grammes of the gas will go into 22.412 litres? Would it in this case be heavier or lighter than air? Would its weight differ from that of air by a small or by a large amount? What would be the case if the formula is N_2O_2? Try some experiment which will decide the question as to its weight. Be careful, however, not to mistake the brown-coloured fumes obtained by the action of air on nitric oxide for the gas itself.

EXPERIMENT 63. Fill a pretty large cylinder with water and invert it over the pneumatic trough, then, as in Fig. 42, bring a small vessel containing air beneath the

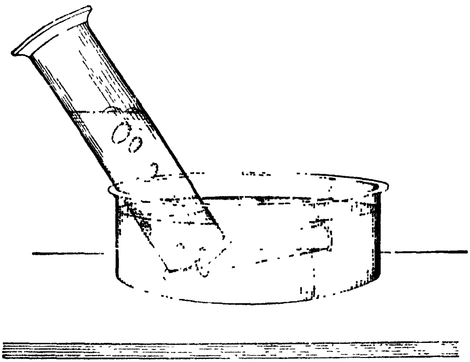


FIG. 42

mouth of the cylinder in such a way as to allow the air to pass into the cylinder. The small vessel should not be more than one-eighth the size of the larger. Introduce five measures of air in this way and mark the height of the water in the cylinder; then introduce two measures

of nitric oxide. What colour do you notice in the cylinder? What evidence have you that the coloured substance is absorbed by the water? Does it colour the water? Test the water in the cylinder with a piece of litmus-paper. Is it alkaline, acid, or neutral? If you do not find that the coloured gas is rapidly removed by the water, cover the mouth of the cylinder with your hand and shake it, being careful that gas does not escape nor air enter, and then put back the cylinder in place over the pneumatic trough. Which has the greater volume, the air at the start or the gas which is left behind at the end? Test the gas left behind by a lighted match or taper. You have already met several gases which affect the taper in the same way. How could you tell which of them it is? What use could you make of your knowledge of the gases originally taken, in helping you to decide the matter? What part of the air was removed by the nitric oxide? Why were red fumes produced at the beginning and not afterwards, in the flask in which nitric oxide was generated? What would be the gas collected in the first cylinder at the beginning of the operation?

Make a solution of ferrous sulphate in water. Which contains the more iron, ferrous sulphate or ferric sulphate? Pour the ferrous sulphate solution into a jar of nitric oxide. What colour is produced? Pour some of the liquid into a test-tube and heat. What change takes place in the solution?

Into the jar of nitrous oxide which you have kept, introduce some nitric oxide. What difference is there between nitrous oxide and oxygen in the action with nitric oxide?

Filter the liquid in the generating flask and evaporate to a small bulk, then allow to cool, and collect the crystals

formed. Dry some of these on blotting-paper. What is the colour? Introduce a few crystals into a dry test-tube and heat. What evidence have you that the crystals contain water? Do the crystals retain their shape after heating? The water found in crystals apparently dry as in this substance is called water of crystallisation, the salt not taking the crystalline form unless water is present. What is the colour of the dried cupric nitrate? Remove some of the cupric nitrate and dissolve in water. What is the colour of the solution? Heat the remainder of the cupric nitrate till fumes come off. What is the colour of the fumes? Continue heating till all fumes cease to be evolved. What is the colour of the residue? Does it dissolve in water? What about the action of hydrochloric acid and nitric acid upon it? What is the substance?

The action of nitric acid upon copper by which nitric oxide is produced may be represented by the equation

$$3\,\mathbf{Cu} + 8\,HNO_3 = 3\,Cu\,(NO_3)_2 + 4\,H_2O + 2\,\mathit{NO},$$

but the nitric oxide is never perfectly pure, and unless care is taken in the conditions a great deal of impurity may be present. For example, after the action has gone on for a considerable time and a good deal of copper nitrate has been produced, nitrous oxide is formed to a great extent, instead of nitric oxide. Why were you told to have all of your vessels ready for collecting the gas rapidly?

Nitric oxide was first collected by Priestley in 1772. He called it nitrous air. It was not till two years afterward that he discovered oxygen, and of course the name nitric oxide was not given until later still.

It is evident that nitric oxide cannot be found free in nature. It can be shown to contain nitrogen and oxygen by passing the gas over heated copper in the same way as was done with air, and in fact any compound or mixture of nitrogen and oxygen may be analysed in this way. By weighing the copper before and after heating, and by measuring the gas, it may be proved that the action is represented by the equation

$$2\,\mathrm{Cu} + 2\,NO = 2\,\mathrm{CuO} + N_2.$$

How does the volume of the nitrogen produced compare with the volume of the nitric oxide used?

Nitric oxide is very sparingly soluble in water and is difficult to condense, the boiling point of the liquid being $-153°$ C.

Nitrogen Trioxide or Nitrous Anhydride. — Nitrogen trioxide, to which the formula N_2O_3 is given, is difficult to prepare, being obtained only at a low temperature, about $-20°$ C. It is a liquid of an indigo blue colour, and decomposes readily into nitric oxide and nitrogen peroxide.

$$\mathrm{N_2O_3} = NO + NO_2.$$

It undergoes decomposition when put into water, but with caustic potash it forms potassium nitrite. The acid that would correspond to potassium nitrite would be nitrous acid. When the name of an acid ends in *-ous*, the name of the corresponding salt ends in *-ite*.

The equation representing the action of nitrous anhydride on caustic potash is

$$2\,\mathrm{KOH} + \mathrm{N_2O_3} = 2\,\underset{\substack{\text{potassium}\\ \text{nitrite}}}{\mathrm{KNO_2}} + \mathrm{H_2O}.$$

The nitrites are somewhat important, and can be comparatively easily obtained, although the corresponding acid and anhydride so readily decompose.

EXPERIMENT 64. Heat some potassium nitrate in a test-tube. Notice that it melts and begins to boil. What is the cause of its boiling? After some time introduce a glowing match into the tube.

What evidence have you that a gas is given off by the potassium nitrate? What is the gas?

The equation representing the reaction is

$$2\,\mathbf{KNO_3} = 2\,\mathbf{KNO_2} + O_2.$$

Why is this equation better than

$$\mathbf{KNO_3} = \mathbf{KNO_2} + O\,?$$

What *volume* of oxygen is represented by O_2? How much potassium nitrate would be required to give that volume? Does the phrase "how much potassium nitrate" imply *weight* or *volume?*

A dilute solution of potassium nitrite mixed with a dilute solution of sulphuric acid, if not allowed to stand too long, may be considered as a solution of nitrous acid, HNO_2. Nitrous acid readily takes up oxygen, forming nitric acid.

EXPERIMENT 65. To a dilute solution of potassium nitrite and sulphuric acid add in a small stream a solution of potassium permanganate. What is the colour of the permanganate? How does the nitrite solution affect the colour? The permanganate is changed by losing its oxygen, and the sulphuric acid present forms potassium sulphate and manganese sulphate. The equation appears somewhat complicated,

$$2\,KMnO_4 + 3\,H_2SO_4 + 5\,HNO_2 =$$
$$K_2SO_4 + 2\,MnSO_4 + 5\,HNO_3 + 3\,H_2O.$$

But though nitrous acid may be *oxidised*, it may also be *reduced*, for it contains oxygen, part of which can be given up to substances requiring it.

Which has the greater amount of oxygen, nitrous oxide or nitric oxide? Which did we find best supports combustion? Which has the more oxygen, nitrous acid or nitric acid?

EXPERIMENT 66. Into a test-tube containing a dilute solution of potassium *nitrate* and potassium iodide pour a dilute solution of sulphuric acid. Into another test-tube containing a dilute solution of potassium *nitrite* and potassium iodide pour a dilute solution of sulphuric acid. What is the appearance in each case?

The mixture of potassium iodide and sulphuric acid acts like a solution of hydriodic acid.

What elements exist in hydriodic acid? Which of them is most ready to combine with oxygen? Which colour is produced by the other component of hydriodic acid? In which of the two experiments above did oxidation of the hydriodic acid take place? Which produced the greater oxidation in the above instance, potassium *nitrate* or potassium *nitrite?* Which is the more active oxidising agent, nitric acid or nitrous acid? How do they compare with nitrous oxide and nitric oxide in this respect?

Nitrogen Peroxide. — EXPERIMENT 67. Heat some lead nitrate in a test-tube till coloured vapours come off strongly. Test the escaping vapours with a glowing splinter. What gas is present, either free or in an easily decomposable compound? The action is represented by the equation $$2\,Pb(NO_3)_2 = 2\,PbO + 4\,NO_2 + O_2.$$

Heat a portion of the lead nitrate till no more fumes are given off. What is the colour of the substance left behind? It is lead oxide. Is lead a univalent or a bivalent element? What is the name of the compound represented by the formula NO_2? How does the volume of this gas compare with the volume of the oxygen produced at the same time?

You will probably not separate the oxygen and the nitrogen peroxide. The separation might be made by passing the mixed gases through a tube surrounded by a freezing mixture. One of the gases would condense. Which one must it be?

Do you have similar results when you heat potassium nitrate and when you heat lead nitrate? Would you think from the result of your experiment that lead nitrite is *more* or *less* stable than potassium nitrite?

Take care to notice as often as you can whether salts of potassium and sodium are more or less stable than the salts of other metals that you come across. You heated copper nitrate in a previous experiment. Is it more like potassium nitrate or lead nitrate? If you do not remember, repeat the experiment.

What arguments have been given for writing the formula of nitrogen peroxide as NO_2, and not N_2O_4?

Nitrogen peroxide uniting with water gives nitrous acid and nitric acid; $2\,NO_2 + H_2O = HNO_2 + HNO_3$. Nitrous acid readily oxidises to nitric. This reaction is used for making nitric acid and nitrates from the atmosphere. Nitric oxide is produced by electric discharges in air, and combining with more oxygen forms nitrogen peroxide, which is converted into nitric acid. Only lately has the process become cheap enough to be commercial.

CHAPTER XII

SULPHUR

Experiments with Sulphur. — EXPERIMENT 68. Drop a few fragments of roll sulphur or a quantity of powdered sulphur into water. Is sulphur heavier or lighter than water? Is there any appearance of solution? If sulphur is not soluble in water or in the saliva, would you expect it to have a taste? Boil the water. Do you notice any change in colour of the sulphur? Does it melt or does it remain solid? Does boiling water appear to dissolve any of the sulphur? Separate the water from the solid sulphur, and find out whether the water contains any sulphur. How can you do this? Would sulphur left in the open air evaporate? If you have sulphur in lumps, try whether it is brittle or malleable, that is, whether it breaks or is flattened by hammering.

Put some dry sulphur into a test-tube and heat. Watch it carefully till it melts. What about the colour? If you have a thermometer which registers up to 150° C., you may try the temperature at which the sulphur melts, but be careful to take out the thermometer before heating the sulphur much higher. How have you already proved that a thermometer which registers 100° C. only could not be used for determining the melting point of sulphur? What is the colour of the melted sulphur? Shake the test-tube. Is the liquid thin and mobile like water, or

thick and viscous like molasses? Now heat still more. What change do you notice in the colour of the sulphur? From time to time shake the tube and see whether the sulphur retains its consistency, that is, whether it remains just as mobile or just as viscous as before. Would you naturally expect heat to make the substance more or less mobile? Is the actual fact what you would have expected? Keep on heating till the sulphur begins to boil, which it will not do till the temperature is higher than can be measured by a mercury thermometer. Now allow the liquid to cool. At one stage it is so viscous that it will pour out of the tube very slowly. At this stage pour it into water. Figure 43 shows the operati n on a larger scale. The sulphur distilled in the retort condenses into liquid form in the neck, and flows into a vessel of water. Take out of the water the sulphur which you have prepared and examine its colour. Notice that it does not feel like the original sulphur. What is the difference? Keep some of this sulphur for a few days in order to see what change takes place. Heat another portion in boiling water for about a quarter of an hour, and rub in your fingers to see how it compares with what it was before heating.

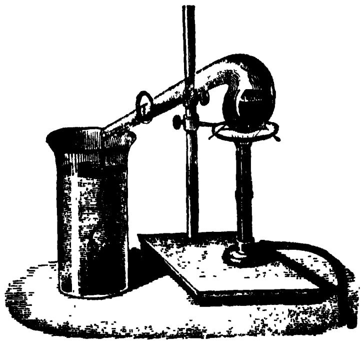


FIG. 43

Heat still another quantity of sulphur in a wide test-tube, and when it is melted allow to cool, watching carefully. Notice the crystals that form. They assume a

needle shape. You will probably not be able to see the crystals for more than a few seconds. Why?

If you have enough sulphur for the purpose, heat 25 or 30 grammes in a clay crucible or any suitable vessel, preferably one that may be broken, or a beaker may be used and the crystals examined from the outside. Allow the melted sulphur to cool, and when about one-quarter has solidified, pierce two holes through the crust on top and pour out the liquid portion. Why should there be two holes? Give a reason why it is better to have them near opposite sides of the vessel, rather than near each other in the middle. After the liquid is poured out, and the crust is broken, the appearance is something like that in the figure (Fig. 44). Examine the crystals and notice their lustre. Keep some of the crystals for a week or two and see if they retain their lustre and colour.

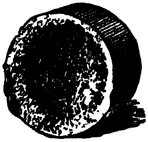


Fig. 44

Dissolve some sulphur in carbon bisulphide, remembering to keep it away from flame, and allow to evaporate slowly. You may find it convenient to put the solution in a test-tube. Would the solution evaporate more rapidly from a test-tube or from a watch-glass? Why? If you try both methods you may see which gives the most perfectly formed crystals. Figure 45 gives the form of a single perfect crystal. Are they the same shape as the crystals you got by cooling the liquid sulphur? When a substance crystallises in two forms, it is called *dimorphous*,

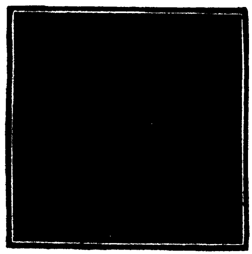


Fig. 45

from the Greek word, which means "two forms." Which form of sulphur remains unchanged the longer? You also obtained a specimen of sulphur somewhat like india rubber, not crystallised at all. It is said to be *amorphous* or without form.

EXPERIMENT 69. Into a test-tube put several crystals of iron pyrites, and heat. Why should the crystals *decrepitate*, that is, break up into smaller crystals with a crackling noise? Would you judge from this action that pyrites is brittle or malleable? Pyrites is sometimes called "fool's gold." Would a piece of gold decrepitate? Gold would act in that respect like silver or copper, so you could experiment with one of these metals. Try hammering some pyrites and see if you were right in your surmise. Heat the pyrites for a minute or two. What evidence have you that pyrites contains sulphur?

Statement regarding the Occurrence, Preparation, and Properties of Sulphur.—Sulphur is found in the neighbourhood of volcanoes, probably produced, in some instances at least, by decomposition of sulphides, in the same way as pyrites was decomposed in your experiment. The largest quantity of sulphur in the market is obtained from mines in the volcanic regions of Sicily. The sulphur is there found mixed with earthy matter, from which it is separated roughly by melting it and allowing it to flow away from the unfused material. It is afterwards purified by distillation. The crude sulphur is heated in a large retort, and the vapours are led into a large chamber as shown in the figure (Fig. 46). The sulphur is first melted in an iron pot, *O*, and runs through a passage not shown in the figure to the retort *G*, whence the vapours pass into the chamber *A*. At first, when the chamber is cool, the

sulphur vapour is condensed into solid material, just as in cold weather water vapour is condensed into snow. The solid sulphur thus obtained is a fine powder, and is called "flowers of sulphur." At a later stage the sulphur collects in liquid form at the bottom of the chamber, and is run out into moulds, forming "roll sulphur."

The compounds of sulphur show that its atomic weight is 32, but the density of the vapour of boiling sulphur is 96 times that of hydrogen at the same temperature; therefore there must be three times as many atoms in the molecule of sulphur vapour as in the molecule of hydrogen, and the molecule of the vapour of sulphur at the boiling point is represented by the formula S_6. At a very high temperature, for instance 1000° C., the density of sulphur vapour corresponds to the formula S_2.

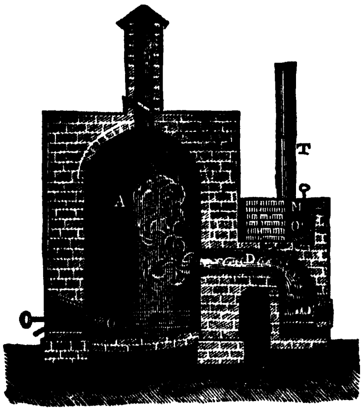


Fig. 46

Sulphur is found not only native but also in combination with many metals. The ores of very many of the ordinary metals are sulphides, — for instance, galena or lead sulphide, sphalerite or zinc sulphide, argentite or silver sulphide; while iron pyrites is a sulphide not much used for obtaining the metal and is therefore not called an ore of iron, though copper pyrites, which contains copper, iron, and sulphur, is one of the most important sources of copper. The sulphates are combinations of metals with

sulphur and oxygen in the proper proportions, the most abundant being gypsum, which is calcium sulphate with water in addition.

Refined sulphur is used in making gunpowder and matches and for vulcanising rubber, while crude sulphur is extensively used for killing the germs which are destructive to grapes.

The specific gravity of the three varieties of sulphur differs slightly and is not far from 2. One crystalline variety melts at 115° C., the other at 120° C.; the liquid boils at 448° C.

Hydrogen Sulphide. — EXPERIMENT 70. Mix seven parts by weight (say grammes) of very fine iron filings with four parts by weight of powdered sulphur. What is the action of a magnet on iron? How could the iron and sulphur in the mixture be separated?

Shake up a portion of the mixture in a test-tube with water and allow to settle. Why do the iron and sulphur form layers? Shake up another portion of the mixture with carbon bisulphide. Which of the two substances is the more affected? Heat the remainder of the mixture in a dry test-tube till it begins to glow, and then remove from the flame. What evidence have you that chemical action goes on even after removal from the flame? When the substance is cool, take it out of the test-tube (you may need to break the tube) and powder it. What evidence have you from the appearance of the substance that it is no longer a mixture of iron and sulphur? Can you separate the two components in the same way as you did before the heating? Would the substance be called a compound or a mixture? The substance produced is ferrous sulphide, FeS.

What happens when sulphuric acid acts on sodium chloride? What might you expect to happen when sulphuric acid acts on ferrous sulphide?

Laboratory Preparation of Hydrogen Sulphide and Experiments with the Gas. — EXPERIMENT 71. Pour a little strong sulphuric acid upon a small quantity of ferrous sulphide. Is the action violent or otherwise? Is there effervescence, as when sulphuric acid acts on sodium chloride? Smell cautiously.

To another small quantity of ferrous sulphide add dilute sulphuric acid and compare results with the action of strong acid. Ferrous sulphate is insoluble in strong sulphuric acid. What bearing has this fact upon the experiments you have tried?

Into a small flask provided with a thistle-tube and delivery-tube, put a few lumps of ferrous sulphide and cover it with water. Pour down the thistle-tube a little strong sulphuric acid, and shake. Add just enough sulphuric acid to cause a liberal supply of gas, and collect two or three small cylinders of it over warm water. Into one cylinder pour a little cold water, place the hand tightly over the mouth of the cylinder, and shake. What evidence have you that the gas is soluble in cold water? Test the solution with litmus to see whether it is acid, alkaline, or neutral. Boil some of the solution for a few minutes. Which smells the more strongly of the gas, the hot water or the cold? In which is the gas the more soluble? Apply a lighted match to another cylinder. Does it burn? Does it support combustion? Hold a cold piece of porcelain, or, better still, a porcelain dish containing water, over the flame. What evidence have you that the gas con-

tains hydrogen? * What evidence have you that there is sulphur in the gas? Does the product of the burning smell the same as the original gas? How does the action on litmus compare in the two cases? It can be proved that the gas contains nothing but hydrogen and sulphur. It is hydrogen sulphide or, as it is frequently called, sulphuretted hydrogen.

It can be decomposed by heat, and the hydrogen produced has exactly the same volume as the hydrogen sulphide taken. But the molecules of hydrogen consist of two atoms, therefore the molecules of hydrogen sulphide must contain two atoms of hydrogen because there are exactly the same number of molecules of hydrogen sulphide as of hydrogen in the same volume. The formula of hydrogen sulphide must therefore be H_2S or H_2S_2 or H_2S_3, etc., and the evidence from the density of the gas is in favour of the formula H_2S. The reaction by which sulphuretted hydrogen is produced is represented by the equation

FeS	+	H_2SO_4	=	$FeSO_4$	+	H_2S.
ferrous sulphide		hydrogen sulphate		ferrous sulphate		hydrogen sulphide

Compare with

2 NaCl	+	H_2SO_4	=	Na_2SO_4	+	2 HCl.
sodium chloride		hydrogen sulphate		sodium sulphate		hydrogen chloride

Is sulphur in hydrogen sulphide a univalent or a bivalent element? What about the iron in ferrous sulphide?

Mix two volumes of sulphuretted hydrogen with three

* If the result of this experiment is not very convincing, burn some of the gas at a jet and hold the porcelain dish over the flame.

volumes of oxygen and apply a lighted taper, taking care to protect yourself from injury by the explosion. The equation shows the reaction

$$2\,H_2S + 3\,O_2 = 2\,H_2O + 2\,SO_2.$$

At ordinary temperatures how would the volume of the products compare with the volumes of the original gases? What difference would there be at a temperature of 110° C.?

EXPERIMENT 72.* Pass sulphuretted hydrogen gas from the delivery-tube successively through a solution of common salt, zinc sulphate, copper sulphate, and arsenic trioxide, in each case adding a little hydrochloric acid to the solution. Notice which solutions are changed in appearance. Which sulphides are insoluble in dilute hydrochloric acid? Have you really had any proof that the precipitates are sulphides? Filter some of the black precipitate, and heat on a piece of porcelain till it dries, and afterwards till it becomes red hot and gives off fumes. What are the fumes? Have you now any proof that the substance is a sul-

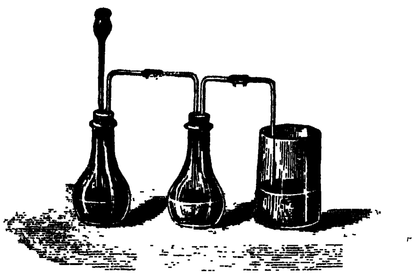


FIG. 47

* Figure 47 shows an apparatus arranged for purifying sulphuretted hydrogen before passing it into a solution to be tested. The wash bottle in the middle contains a little water and frees the gas from any impurity carried over mechanically from the generating flask. You may not find it necessary to use the wash bottle.

phide? The precipitates obtained by the action of sulphuretted hydrogen are usually sulphides. Now add to each of the liquids, whether containing a precipitate or not, more than enough ammonia to neutralise all the acid. Which sulphides are insoluble in a liquid containing free ammonia? A number of other metals are similar to sodium, zinc, copper, and arsenic, and the experiment you have just tried is an example of what is constantly done in the laboratory. When one wishes to know what metal is in a substance, it is sometimes possible to separate the metal itself and thus to identify it. For instance, iron could be obtained from hematite. But it is usually much more easy to produce a compound of the metal which can be easily recognised as a compound of that metal, and of no other, and so in chemical analysis it is much more frequently the case that substances are tested by getting them into the liquid form and then adding certain reagents in order to find out the constituents. Ammonia, for example, is a good test for copper; potassium ferrocyanide is a good test for iron. But it is easily seen that it would be a great trouble to apply each test separately till the right one was discovered, if one had no idea what metal to look for. It has been found very convenient to use sulphuretted hydrogen to divide the metals into smaller groups. Some metals give a precipitate with hydrogen sulphide in an acid solution, some give a precipitate in an alkaline solution, and some do not give a precipitate in either acid, alkaline, or neutral solution. So it is easily seen that the list of metals is broken up into smaller groups and that by the addition of sulphuretted hydrogen a good deal may be learned. Hence, notwithstanding the disagreeable odour of the gas, it is constantly

employed in an analytical laboratory. After a while one becomes accustomed to the smell and does not find it disagreeable, and some people even learn to like it.*

We have seen that hydrogen sulphide has the formula H_2S, corresponding to the formula H_2O; and though sulphur and oxygen are so dissimilar in appearance and in physical properties, they form compounds which have many analogies.

Hydrogen and sulphur may be made to unite directly by raising them to the proper temperature; but the reaction is not nearly so energetic as between hydrogen and oxygen, and the compound produced is not so stable. In heating organic substances containing hydrogen and sulphur, sulphuretted hydrogen is often produced, just as in heating organic substances containing hydrogen and oxygen, water is often produced. Sulphuretted hydrogen is found in the so-called sulphur springs, whose characteristic odour and taste are due to the presence of the gas in solution.

Sulphuretted hydrogen can be compressed into a liquid at the ordinary temperature by a pressure of about seventeen atmospheres, and can be liquefied at atmospheric pressure by cooling down to $-62°C$. It freezes at $-85°C$. Sulphuretted hydrogen is poisonous and should not be inhaled, except in very small quantities.

Laboratory Preparation of Sulphur Dioxide and Experiments with the Gas. — EXPERIMENT 73. Burn some sulphur in a jar of air, keeping the jar covered so as to prevent the escape of fumes. Pour a little water into the jar and shake, and in this way obtain a solution. Test

* The writer knew a man who was so fond of the smell of the gas that he one time inhaled so much of it from a bottle that he fell insensible.

with litmus; smell. Add some barium chloride, along with a little hydrochloric acid, to a portion of the solution. To another part of the solution add a fifth of its volume of concentrated (strong) nitric acid and then barium chloride solution.

In one case there should be no precipitate, or only a slight one; in the other case there should be a white precipitate. The white precipitate is given by sulphuric acid.* The solution which did not give a precipitate was sulphurous acid. Which of these acids has the most sulphur in proportion? Which the most oxygen? Is nitric acid an oxidising or a reducing agent? This reaction is very important and should be remembered, as it is made use of on the manufacturing scale.

What is the action of dilute sulphuric acid on zinc? What is the action of nitric acid on copper?

EXPERIMENT 74. Into a flask, as shown in the figure (Fig. 48), put some copper wire or filings, and cover with strong sulphuric acid. Heat carefully over a wire gauze, or, still better, on a sand bath, an iron plate containing sand. Be very careful to have the apparatus so arranged that if the flask should happen to break, the sulphuric acid would do no harm. Hot sulphuric acid causes a terrible burn. Notice the ebullition of gas and collect a cylinder of it by downward displacement, covering the cylinder with a glass plate, and make a solution by passing a stream of the gas into water. Take great care that the water does not run back into the strong acid.

* Such a small quantity of sulphuric acid gives a visible precipitate that, unless the deflagrating spoon is clean, some sulphate may be produced. The sulphur even may possibly contain some sulphate. It is possible that a little sulphur trioxide may be formed in the burning, and it, with water, gives sulphuric acid.

The reaction by which the gas is made may be represented by the equation

$$\mathbf{Cu} + 2\,H_2SO_4 = CuSO_4 + 2\,H_2O + \mathit{SO_2}.$$

What have you learned about the specific gravity of the gas? Does it support combustion? Does it burn? What is the difference between the action of nitric acid on cupric oxide and on copper? What is the difference between the action of sulphuric acid on cupric oxide and on copper? Show that in the latter case sulphuric acid has an oxidising action, while in the former it has not.

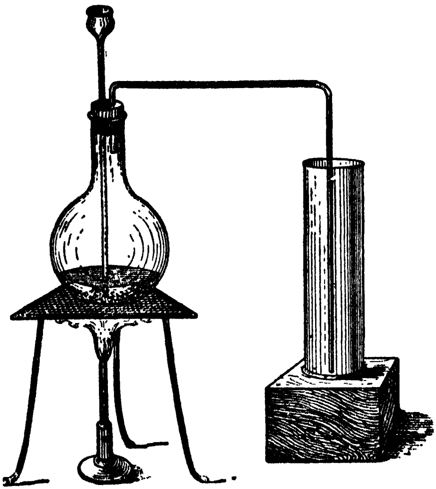


FIG. 48

Assuming that the equation represents the facts, how much of the sulphur is obtained in the form of sulphur dioxide? What becomes of the rest of the sulphur? Is the action more like that of dilute sulphuric acid on zinc or of nitric acid on copper?

How many atoms of oxygen are represented as existing in a molecule of sulphuric acid? How many of these would be necessary to combine with all of the hydrogen? How many does that leave for the sulphur? In sulphur

dioxide, is there a larger or smaller proportion of oxygen for the sulphur than in sulphuric acid? If sulphur dioxide were dissolved in water, would oxygen need to be added or to be taken away in order to produce sulphuric acid? Pour a little iodine solution into some solution of sulphur dioxide. What is the colour of the iodine solution? What is the colour of the solution produced by the addition of it to sulphur dioxide solution? Add some barium chloride and hydrochloric acid to the solution thus obtained. What evidence have you of the presence of sulphuric acid? Sulphurous acid in this case takes up oxygen, and is called a reducing agent. Quantitative experiments show that given the proper conditions the reaction is represented by the equation

$$I_2 + H_2O + SO_2 = 2HI + H_2SO_4.$$

How many grammes of iodine could be decolourised by 40 grammes of a one per cent solution of sulphur dioxide? What is it that supplies oxygen in this reaction? What becomes of the rest of the compound from which the oxygen is obtained? Why is the iodine said to be reduced?

Sulphur dioxide in water is sometimes used as a bleaching agent for wool, straw, and other materials, for which chlorine is unsuited. It is also used as a disinfectant, sulphur being frequently burned in houses where there has been an infectious disease.

That the composition of the gas is actually that which the name implies may be proved by experiment.

EXPERIMENT 75. Fill with mercury a tube of the shape shown in the figure (Fig. 49) and of about half-inch bore, and invert in a trough containing mercury. Introduce a

small piece of sulphur, and then enough oxygen to approximately half fill the tube. Put a mark to show the height of the mercury, then heat the sulphur. Notice that it burns and that the mercury goes down in the tube. Why should it do so? When the combustion is complete, allow to cool to the original temperature. The volume should be the same as that of the oxygen. How many atoms are there in the molecule of oxygen? How many atoms of oxygen must there be in the molecule of the compound produced by burning sulphur in oxygen? Does this distinguish between the formulæ SO_2, S_2O_2, and S_3O_2? If the formula is SO_2 and the atomic weight of sulphur is 32, how many grammes of the gas will go into 22.412 litres? How many grammes will occupy the same volume if the formula is S_2O_2? The density of sulphur dioxide compared with air as unity is 2.2 approximately. Which of the above formulæ is the proper one?

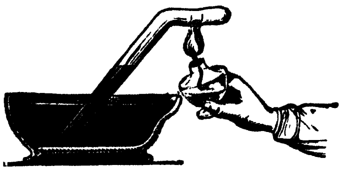


FIG. 49

Sulphur dioxide can be condensed at atmospheric pressure by cooling to − 8° C., and is easily kept in liquid form in small sealed glass tubes at the ordinary temperature. The solution of sulphur dioxide in water is practically sulphurous acid, though the acid has never been obtained without water. The formula of the acid would be H_2SO_3, and compounds such as potassium sulphite K_2SO_3, in which hydrogen is replaced by metals, are easily obtained. As nitrites are salts corresponding to nitrous acid, so sulphites (contraction for sulphurites) are salts corre-

sponding to sulphurous acid. The sulphites are employed as reducing agents, neutralising, for instance, excess of chlorine used for bleaching, just as in your experiment the colour of iodine was discharged by the action of sulphurous acid.

Sulphuric Acid. — You have used sulphuric acid almost from the very beginning of your work in chemistry, and you have seen something of its importance in the laboratory. It is quite as important in industrial chemistry, that is, in the processes of chemical manufacture on the large scale. In Great Britain alone 1,000,000 tons is produced every year, and in the United States a still larger amount. Sulphuric acid is found to a slight extent in volcanic regions. Gypsum is found in large quantities, but it is not easy to make sulphuric acid from it. Why could you not use hydrochloric acid or nitric acid to drive out the sulphuric acid? Sulphur burns in air, but it forms sulphurous anhydride, and that with water would form sulphurous acid, while sulphuric acid contains more oxygen. This oxygen can be added by allowing the sulphurous acid solution to stand in the presence of air for a long time, say for months or years, but this is not a practical method of manufacture.

Sulphuric Acid Manufacture. — The experiment you tried of adding nitric acid to sulphurous acid solution, illustrates the method used on the large scale. Sulphur dioxide is produced either by burning sulphur, or by *roasting* (that is, heating in the presence of a large supply of air) iron pyrites, or some other sulphide.

The sulphur dioxide is brought into large chambers made of lead, the cheapest material that will withstand the action of the acid ; steam, air, and nitric acid are also

introduced into the lead chambers. The nitric acid oxidises the sulphur dioxide in the presence of water, as we saw in our experiments, and is itself reduced to an oxide of nitrogen which takes up more oxygen from air introduced with it, and becomes a higher oxide of nitrogen, that is, an oxide containing a larger proportion of oxygen. This higher oxide is again reduced by more sulphur dioxide in the presence of water, more sulphuric acid is produced, and more of the lower oxide of nitrogen, which again goes through the same round as before.

Theoretically, therefore, there need be only a small amount of nitric acid introduced at the beginning of the operation, and afterwards only a supply of sulphur dioxide, water, and air. Practically, some loss of the oxide of nitrogen occurs, and hence nitric acid must be constantly supplied, though not in large quantity.

The following equations give an indication of the character of the changes that occur, though they do not represent perfectly the complicated course of the reaction:

$$2\,HNO_3 + 2\,H_2O + 3\,SO_2 = 3\,H_2SO_4 + 2\,NO$$
$$NO + O = NO_2$$
$$H_2O + NO_2 + SO_2 = H_2SO_4 + NO$$

The lead chambers* are very large, some of them having a capacity of 80,000 cubic feet.

The strongest acid usually sold has a density of 1.84; chamber acid has a density of 1.6, the density of water being unity. The chamber acid is concentrated by boiling

* The lead chamber must be large, otherwise the gases do not mix properly. Such chambers are expensive, and lately towers of less capacity, but with a special arrangement for mixing the gases, have been introduced with marked success.

in shallow lead pans till it has a density of 1.7. It cannot be concentrated any farther in lead dishes, because stronger acid attacks lead; hence it is evaporated in large glass flasks or in platinum dishes, as shown in Fig. 50, or in

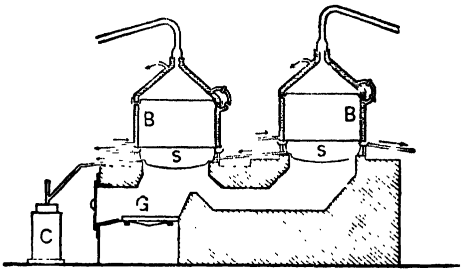


FIG. 50

some cases in cast-iron stills, since, though dilute sulphuric acid acts on iron, strong acid does not. Compare your results obtained by treating ferrous sulphide with concentrated and dilute sulphuric acid.

When sulphur dioxide and oxygen are passed over heated platinised* asbestos, as shown in Fig. 51, the two unite to produce sulphur trioxide SO_3. Sulphur trioxide uniting with water forms sulphuric acid. The figure represents a current of air passing through a solution of sulphur dioxide, carrying some of it to the platinised asbestos, where it is changed to trioxide, after which it is absorbed in water.

This method of making sulphuric acid has now become

* Platinised asbestos is prepared by moistening asbestos in a solution of platinic chloride, adding to it ammonium chloride solution, drying, and igniting. The chloride is decomposed, chlorine being given off, and platinum remaining upon the asbestos.

of commercial importance, and may ultimately replace the older method. It is much simpler than the method with lead chambers, but there were difficulties in carrying on the process on the large scale which have now been overcome.

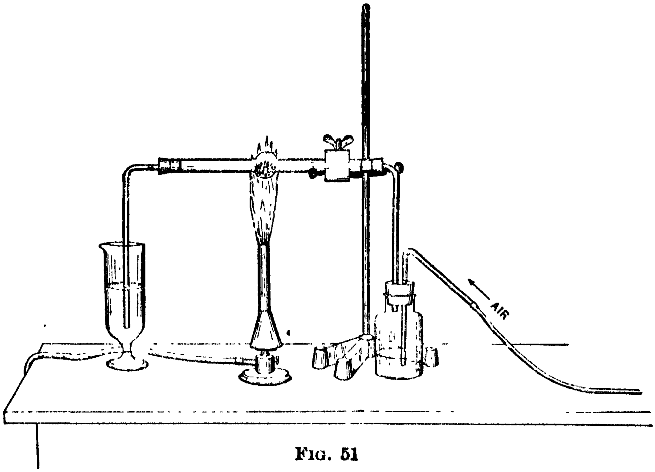


FIG. 51

Sulphuric acid is often called oil of vitriol, because it was first made from ferrous sulphate or green vitriol.

Experiments with Sulphuric Acid. — What evidence have you had that sulphuric acid has a great affinity for water?

EXPERIMENT 76. Heat a piece of sugar in a dry test-tube. How can you show that water exists in sugar or is produced in the operation of heating? What is left behind when the water is distilled off? Is the distillation of water from sugar a case of simple *distillation*, or of *destructive* distillation? To another piece of sugar add concentrated sulphuric acid. What evidence have you now that sulphuric acid has been effectual in removing

water from sugar? Sugar contains hydrogen and oxygen in just the right proportions to form water, the remainder of the substance being charcoal or carbon.

Pour upon a piece of wood in a test-tube some strong sulphuric acid. What is the effect? Write on paper with dilute sulphuric acid, and hold above a flame so as to evaporate the water from the acid, but far enough away that the heat of the flame will not burn the paper. What happens to the paper where the acid was put upon it?

It can be easily seen from the formula H_2SO_4, got as the result of *analysis* or of *synthesis*, that sulphuric acid contains the elements of water. At a high temperature the acid breaks up into two parts, water vapour and sulphur trioxide, H_2O and SO_3. This is what is seen when sulphuric acid boils. Heat a few drops in a tube till it volatilises. The fumes seen are sulphur trioxide. Sulphur trioxide is called sulphuric anhydride, just as sulphur dioxide is called sulphurous anhydride. What is meant by the term anhydride?

EXPERIMENT 77. To a solution of sulphuric acid add a dilute solution of caustic soda till the acid is just neutral. How can you tell when this point is reached? Evaporate the solution to dryness. What is the substance left after evaporation?

The action is represented by the equation

$$2\,NaOH + H_2SO_4 = Na_2SO_4 + 2\,H_2O.$$

Compare this with the equation for the action of hydrochloric acid and caustic soda,

$$NaOH + HCl = NaCl + H_2O.$$

How many molecules of the alkali (or base) are required for one molecule of hydrochloric acid? How many for one molecule of sulphuric acid? Hydrochloric acid is called a monobasic acid, and sulphuric acid a dibasic acid.

Test the sodium sulphate with a little barium chloride solution, adding a few drops of hydrochloric acid.* Do the same with sodium chloride. All soluble sulphates act in the same way with barium chloride, and a *sulphate* is distinguished by this test.

There are a number of other acids containing hydrogen, sulphur, and oxygen, but they are not nearly so important as sulphurous acid and sulphuric acid.

Several years ago Sicily produced nearly all of the world's sulphur, but now very large quantities are obtained in the United States, chiefly in Louisiana. Steam is forced down, through pipes similar to those employed in oil wells. Steam when under pressure can be heated to a high temperature, and for this purpose the steam is heated sufficiently to melt the sulphur, which is in beds at a considerable depth in the earth. The melted sulphur is forced to the surface by the steam pressure through a small pipe inside the steam pipe.

The production of sulphur in the United States has increased from less than 7000 tons in 1901 to 232,000 tons in 1905 and the import of sulphur from abroad has decreased during the three years 1903 to 1905 by more than 100,000 tons.

* The reason hydrochloric acid is added is that many compounds of barium are insoluble in alkaline or neutral solution, but not in acid.

CHAPTER XIII

THE PHOSPHORUS GROUP OF ELEMENTS

Experiments with Phosphorus. — EXPERIMENT 78. Cut off a small piece of phosphorus under water, and dry it on blotting-paper. Take the same precautions as when you were working with phosphorus before, because burns with phosphorus are more painful than ordinary burns.

Rub your penknife, or any piece of iron, two or three times quickly on piece of wood, and touch the phosphorus with it. Put a moistened paper in the fumes and taste it. What reason do you see for burns produced by phosphorus being specially painful? Notice the smell of the fumes from phosphorus. The odour is somewhat similar to that of garlic.

EXPERIMENT 79. Place a piece of filter-paper upon a tripod as in the figure (Fig. 52), or on the ring of a retort stand. Dissolve some dry phosphorus in carbon bisulphide, and pour enough on the filter-paper to moisten it. Allow to stand for two or three minutes till the carbon bisulphide is evaporated. The phosphorus left behind should take fire. Notice whether the paper takes fire from the burning phosphorus. Which has the greater surface, the small piece of phosphorus you dissolved, or the

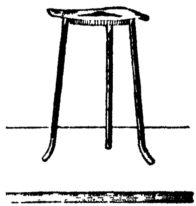


FIG. 52

paper moistened by its solution in carbon bisulphide? In which case would the oxygen of the air have a greater opportunity to act on the phosphorus? Which would you expect to take fire the more readily?

Upon a piece of filter-paper, in the same way as before, place less than a teaspoonful of dry potassium chlorate finely powdered. Pour upon the chlorate enough of the solution of phosphorus in carbon bisulphide to moisten it, and allow to remain for a few minutes, keeping at a distance of several feet, because the combustion of the phosphorus takes place with explosion. Why should the phosphorus burn more violently when put upon the potassium chlorate, than when put on paper alone? What experiments did you do some time ago to show the action of potassium chlorate on combustible substances?

EXPERIMENT 80. Put a piece of phosphorus into a test-tube with water, as shown in Fig. 53. Fit into the test-tube a cork with a tube drawn out to a narrow opening. Boil the water. Does the phosphorus melt below the boiling point of water or not? How does it compare in this respect with sulphur? What evidence have you that phosphorus vapour passes out through the tube with the steam? If possible, do the experiment in a dark room and

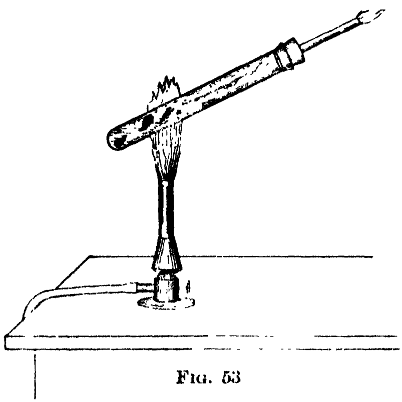


FIG. 53

notice the colour that appears at the opening from which the steam issues. Withdraw the test-tube from the flame and notice that air runs back into the tube. How is this shown?

EXPERIMENT 81. Put a piece of phosphorus into a cylinder and notice that it glows (this can be seen only in the dark). Then dip a piece of paper or cloth into turpentine and introduce into the cylinder with the phosphorus. If the vapour of turpentine covers over the phosphorus, would you expect the latter to continue to glow? Does the phosphorus continue to glow? The phosphorus you have been working with is ordinarily called yellow phosphorus. It must be kept in water to prevent its catching fire, it dissolves in carbon bisulphide, and it is very poisonous. There is another form of phosphorus with different properties.

EXPERIMENT 82. Into a small bottle introduce a piece of phosphorus, and then a very small fragment of iodine, taking care that they touch. Cover the bottle loosely. In a few moments there should be a flash of flame. Pour some water into the bottle and wash out the phosphorus. What colour has it? What other difference in appearance has it? Does it dissolve in carbon bisulphide? Heat it in water and see if it melts. Does it give off the same kind of vapour as before when the water is boiling? The phosphorus thus obtained is called red phosphorus. It does not crystallise, whereas yellow phosphorus may be obtained in the form of crystals. Red phosphorus is therefore sometimes called amorphous phosphorus. It is not poisonous,* and does not ignite so readily as yellow phosphorus. In this case we have two allotropic forms of

* The amorphous phosphorus should not be tasted, however, because there may be some of the poisonous variety still remaining.

one element. What other examples of allotropic forms have you had?

The vapour of phosphorus weighs 62 times as much as the same volume of hydrogen, and as the molecular weight of hydrogen is 2, the molecular weight of phosphorus is 124. But it can be proved that the atomic weight of phosphorus is 31; therefore the molecule of phosphorus vapour has four atoms, and the formula is P_4. We have now met elements having two atoms in the molecule, one which contains three, one with six, and one with four.

Hydrogen Phosphide. — EXPERIMENT 83. Fit up a flask of a capacity of about 200 c.c., as in the figure (Fig. 54).

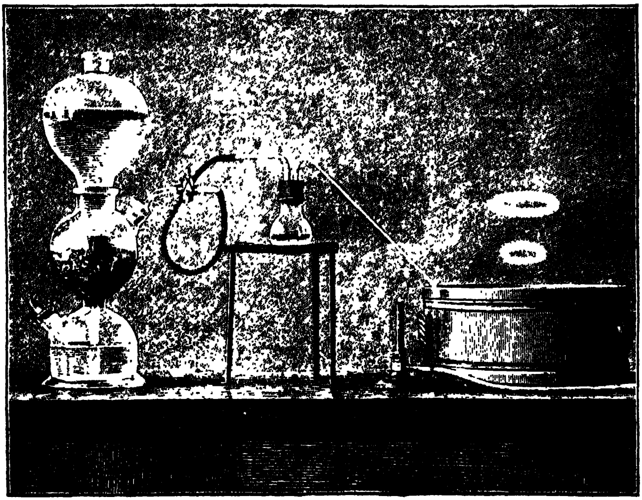


FIG. 54

Into the flask put a few pieces of phosphorus about the size of a pea, and then put in enough concentrated solu-

tion of caustic soda to fill one-third of the flask. Pass hydrogen from the hydrogen apparatus till the air is all driven out from the flask.* Stop the stream of hydrogen and heat the flask till gas comes off. Notice the bubbles which escape after a time from the tube which dips under the water. Notice the smell, but be careful not to inhale the gas, for it is very poisonous, and will soon give a headache. If the bubbles do not take fire of themselves when reaching the surface of the water, apply a light to them in order to avoid the escape of any of the poisonous gas into the air. Before long, the bubbles will take fire, and, owing to the way in which they escape from the water into the air, the smoke has a ring shape and moves with what is called a vortex motion. If two rings follow in quick succession, you may be able to see the foremost ring widen out and go slowly, while the hindmost ring becomes

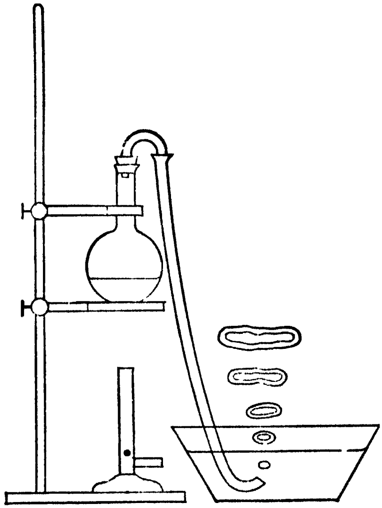


FIG. 55

* The apparatus may be so arranged that instead of hydrogen being passed into the flask a few drops of ether may be added. Only a few drops should be added, else the bubbles of hydrogen phosphide will not inflame spontaneously. Figure 55 is a diagrammatic sketch showing this arrangement.

smaller, goes faster, and passes through the other ring. Of course, you cannot hope to see this phenomenon if there is a draught.

The gas produced in the reaction is called hydrogen phosphide, or phosphine. It is, in many respects, similar to ammonia, and, as the formula of ammonia is NH_3, so the formula of phosphine is PH_3, and, though phosphine is not strongly alkaline like ammonia, it forms some salts called phosphonium salts similar to ammonium salts. There is, for instance, phosphonium iodide, PH_4I, which corresponds to ammonium iodide, NH_4I, but it is not nearly so stable, being decomposed by water.

The phosphine obtained as described is not perfectly pure. Perfectly pure phosphine does not take fire spontaneously. A small quantity of another phosphide of hydrogen gives it the property of spontaneous ignition.

When phosphine is produced by the action of caustic soda on phosphorus, a compound containing phosphorus and sodium, called sodium hypophosphite, is left in solution.

The reaction is for the most part represented by the following equation, though some other reactions go on to a slight extent that are not represented by it:

$$3\,NaOH + \mathbf{P_4} + 3\,H_2O = 3\,\underset{\text{sodium hypophosphite}}{NaH_2PO_2} + \boldsymbol{PH_3}.$$

What proportion of the phosphorus employed forms phosphine?

Compare the two equations

$$2\,\boldsymbol{PH_3} + 4\,O_2 = 2\,\mathbf{H_3PO_4}$$
$$2\,\mathbf{P} + 5\,O = \mathbf{P_2O_5}.*$$

* It will be noticed by the reader that these equations are not molecular, and we could not calculate volumes in the ordinary method from them.

For which is the more oxygen required, for the phosphorus or for the phosphine containing the same amount of phosphorus? Phosphine is said to be a more reduced product than phosphorus. Why? On the other hand, in sodium hypophosphite the phosphorus is oxidised to a certain extent, so that three-fourths of the phosphorus is oxidised by the caustic soda, and one-fourth is reduced during the process. If, instead of caustic soda, lime mixed with water is used, calcium hypophosphite is obtained, and from it hypophosphorous acid may be prepared. Hypophosphorous acid is not volatile, and therefore cannot be prepared by distilling the salt with sulphuric acid; but calcium sulphate is nearly insoluble, and when calcium hypophosphite in solution is treated with sulphuric acid, calcium sulphate separates as a solid, and the solution of hypophosphorous acid is obtained. This method of preparation of acid is interesting, being different from those which you have had.

Phosphoric Acid. — When phosphorus is burned in air, it combines with oxygen, forming phosphorus pentoxide, P_2O_5. This substance, which you have so many times seen as a white smoke, combines very readily with water, and forms phosphoric acid, so that phosphorus pentoxide is called phosphoric anhydride. It can combine with water in three proportions, shown by the formulæ H_2O, P_2O_5; $2 H_2O, P_2O_5$; and $3 H_2O, P_2O_5$. (Remember that this mode of writing means that the 2 and 3 belong only to the H_2O, and not to the P_2O_5.) It might be thought that when these acids are put into a large quantity of water they would all be the same, but they are not. As they are all derived from phosphoric anhydride, they are all phosphoric acids. They may be written HPO_3 (which

is just half of H_2O, P_2O_5), $H_4P_2O_7$, and H_3PO_4. The last is the most important. It can be obtained in the form of large crystals which readily take up water, and are nearly always moist. The crystals are therefore said to be *deliquescent.* As it is the most important of the three phosphoric acids, it is called orthophosphoric acid, the prefix being derived from a Greek word meaning *right.* In the molecule there are three hydrogen atoms, any or all of which may be replaced by metal, so that there are three different salts of sodium, NaH_2PO_4, Na_2HPO_4, and Na_3PO_4. Orthophosphoric acid is therefore a *tri*basic acid, just as sulphuric acid is a *di*basic acid because it forms salts $NaHSO_4$ and Na_2SO_4. When the hydrogen is not all replaced in an acid, the salt is often called an acid salt, and it frequently reddens litmus-paper; thus sodic hydric sulphate, $NaHSO_4$, reddens litmus. In the same way, sodic dihydric phosphate (what is the meaning of the term?), NaH_2PO_4, is acid, but disodic hydric phosphate, though its formula represents an acid salt, does not redden litmus nor turn it blue, and is, therefore, a neutral phosphate, while trisodic phosphate is alkaline.

One atom of calcium is equivalent to two atoms of sodium, as is shown by the formula NaCl for sodium chloride, and $CaCl_2$ for calcium chloride; therefore the calcium salt which corresponds to NaH_2PO_4 is $CaH_4P_2O_8$, or, as it is frequently written, $CaH_4(PO_4)_2$. This calcium acid phosphate, commercially known as superphosphate of lime, is an important substance, being used very largely as a fertiliser. The substance $Ca_3(PO_4)_2$, corresponding to Na_3PO_4, is a common mineral, and the reason why it is not used as a fertiliser is because it is not soluble in water, and plants cannot make use of food except as gas or in solution.

Action of Heat on Phosphoric Acid. — When orthophosphoric acid is heated to a little over 200° C., it loses water, and is changed into another acid called pyrophosphoric acid, because produced by heat, the prefix being derived from the Greek word for fire.

$$\underset{\text{orthophosphoric acid}}{3\,H_2O,\ P_2O_5} = H_2O + \underset{\text{pyrophosphoric acid}}{2\,H_2O,\ P_2O_5}.$$

This has different physical properties from orthophosphoric acid, — having a different specific gravity, for instance, — and it gives different results with various chemical reagents.

When pyrophosphoric acid is heated still more strongly, so that the dish becomes red, more water is lost, and a substance is left behind called metaphosphoric acid. The prefix *meta* indicates that it is an acid *in addition to* the others.

$$2\,H_2O,\ P_2O_5 = H_2O + \underset{\substack{\text{metaphosphoric}\\ \text{acid}}}{H_2O,\ P_2O_5}.$$

We do not really know what the molecule of the phosphoric acids is, and we write H_3PO_4, $H_4P_2O_7$, and HPO_3, or $3\,H_2O,\ P_2O_5$, $2\,H_2O,\ P_2O_5$, and $H_2O,\ P_2O_5$, just to suit our convenience for the purpose we have in view; some of the chemical relations being shown better by one formula, and some by another. The last form, for example, is best, if we wish to show the acids as compounds of phosphoric anhydride with water.

No amount of heat will drive off the last portion of water from metaphosphoric acid, so that we see again how firmly phosphoric anhydride unites with water, because sulphuric acid, even though having so great an affinity

for water, can be broken up by heat into water vapour and sulphuric anhydride.

Phosphorous and Hypophosphorous Acids. — In all of the phosphoric acids there is just the same amount of oxygen for the phosphorus, because they are all derived from the one anhydride P_2O_5. But there are other acids of phosphorus which contain less oxygen, and, therefore, more phosphorus in proportion. What would you expect an acid to be called which contains more phosphorus than phosphoric acid? Orthophosphoric acid has the formula H_3PO_4; phosphorous acid has the formula H_3PO_3. We have already learned about hypophosphorous acid, which contains less oxygen than phosphorous acid, as is implied by the prefix. Its formula is H_3PO_2. Phosphorous acid, as well as hypophosphorous acid, is ready to take up oxygen and become phosphoric acid, and is therefore a reducing agent.

Statement regarding the Occurrence, Preparation, and Properties of Phosphorus. — Since hypophosphorous and phosphorous acids are so ready to take up oxygen, they are never found in nature, and since phosphoric acid is a strong acid it also does not occur naturally uncombined, but the phosphates are very important compounds. Calcium phosphate $Ca_3(PO_4)_2$, usually combined with fluoride, is the most common and the most important. Phosphorus is made from it or from the calcium phosphate which forms the larger portion of bone ash, the residue left when all of the organic matter is burnt off from bones.

Though phosphorus was discovered about 1675, it was obtained by a very difficult process, and was for a century only a curiosity. In 1775 Scheele, the same man who discovered chlorine, made it from bone ash by a process which, till lately, has been exclusively used. The process

is complicated, and is being now replaced by heating the phosphate with carbon in an electric furnace. At that very high temperature carbon is able to take oxygen from the phosphorus, the phosphorus distils in the form of vapour, and is condensed. The ordinary or yellow phosphorus has a specific gravity 1.82, melts at 43° C. under water, and more easily when dry, and distils at 269° C. It is very poisonous, 0.15 grammes being a fatal dose. Workmen employed in factories where it is made or used are liable to decay of the bones, so that the industry is a very unhealthy one. Red or amorphous phosphorus made by heating ordinary phosphorus in an atmosphere of nitrogen to a temperature of 250° C., has a specific gravity 2.25. It is not affected by air at the ordinary temperature, and so does not need to be kept under water. At a moderately high temperature, which varies according to circumstances, it changes into the yellow modification.

Phosphorus is largely used in the manufacture of matches. Friction matches were first made in 1827, originally without phosphorus, but very soon phosphorus was introduced. The tips of matches usually contain phosphorus mixed with some oxidising substance, with glue, and with some neutral substance. The mixture must be such as to ignite with the proper amount of friction, but not to be too readily inflamed. Since yellow phosphorus is poisonous, and is also readily inflammable, safety matches are made having no phosphorus in the composition of the heads of the matches themselves, but having red phosphorus in the composition on the surface of the box. The matches take fire only when rubbed upon the prepared surface.

In France, phosphorus has been lately replaced by

phosphorus sulphide, which is said to be much superior to phosphorus alone, because not poisonous. The French government offered a prize for the best substitute for phosphorus in the manufacture of matches, and the reward was given for the proposal to use phosphorus sulphide.

Arsenic. — EXPERIMENT 84. Into a closed glass tube, as shown in Fig. 56, of less than half a centimetre bore and two or three centimetres length, put a small fragment of arsenic trioxide (say the size of a pin head), and then a piece of charcoal small enough to allow it to slip down the tube easily, but large enough nearly to block the passage. Heat the charcoal till it is red, then heat the arsenic trioxide. Notice in the tube a ring of bright metallic lustre forming a mirror. What substance do you already know for which carbon has a great affinity? The mirror is formed of the element arsenic; the trioxide, often called white arsenic, is a compound of arsenic and oxygen, whose composition corresponds to the formula As_2O_3. The element arsenic has a metallic appearance, though in many respects it is unlike a metal.

FIG. 56

EXPERIMENT 85. Put a little powdered arsenic trioxide into water. Does it dissolve readily? Does it dissolve at all? In order to answer this question, filter, and divide the filtrate into two parts. Pass a stream of sulphuretted hydrogen through one portion for a couple of minutes. Is there any precipitate? To the other portion of the filtrate add hydrochloric acid, and then pass sulphuretted hydrogen as before. Is there a precipitate? Heat both liquids. Make a comparison between your results in all stages of your parallel experiments.

Arsenic trioxide has the percentage composition corresponding to the formula As_2O_3. Assuming the atomic weight of arsenic as 75, what weight of vapour of the trioxide should go into 22.412 litres, if the substance could be obtained as vapour having atmospheric pressure at 0° C? It is found by experiment that the vapour is 198 times as heavy as hydrogen at the same temperature. Does this correspond to the formula As_2O_3 or As_4O_6?

Arsenic trioxide does not readily combine with water, but there are salts which would correspond to an acid so obtained, and hence arsenic trioxide is often called arsenious anhydride and the salts are arsenites. A corresponding oxide of phosphorus is known, but is unimportant, while arsenic pentoxide, As_2O_5, which corresponds to phosphorus pentoxide, P_2O_5, is much less stable than the latter and readily decomposes into arsenic trioxide and oxygen, so that the phosphorus and arsenic oxides do not correspond as regards stability. Phosphates and arsenates are however, very similar in their chemical relations.

White arsenic is very poisonous, the fatal dose being about the same as that of phosphorus. In very small doses, such as $\frac{1}{50}$ of a grain, it is used as a medicine. It has a good effect on the skin and on the digestion, but it should never be taken unless by a doctor's advice. The habit grows, and as the system becomes accustomed to its use, larger doses can be taken. But if the attempt is made to discontinue its use, all the effects of arsenical poisoning are experienced. Peasants in mountainous districts sometimes use arsenic in order to strengthen their power of breathing when climbing. It is one of the poisons most frequently administered, probably because it is almost tasteless. It is, however, one of the most easily

detected. It preserves the tissues of the stomach and may be detected years after the death of the poisoned person. The best antidote for arsenic is a mixture of magnesia and ferric hydroxide, because arsenic forms an insoluble compound with these substances.

EXPERIMENT 86. Make hydrogen in the usual way with zinc and sulphuric acid, the delivery-tube being in the form shown in Fig. 57, so that the hydrogen may be burned as it escapes. Do not apply a light till you have made sure that air is all driven out of the flask. Why? When the hydrogen is burning, notice the colour of the flame. Hold in the flame a porcelain evaporating dish containing water. Notice whether there is any deposit on the dish. If there is not, you may be sure that you have no arsenic in the materials with which the hydrogen is prepared. This is a very important precaution, because both zinc and sulphuric acid sometimes contain arsenic. If there is no deposit on the dish, introduce through the thistle-tube a few drops of arsenic dissolved in hydrochloric acid.* Does the flame become larger or smaller? What is its colour? Hold in it a porcelain dish as before and observe the character of the deposit formed on the dish. It should be of a grayish colour and look like a mirror. This is called Marsh's test, from the name of the man who first used it.

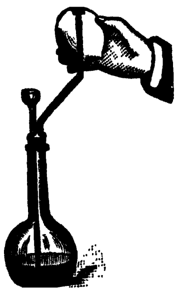


FIG. 57

In the case of arsenic poisoning, the arsenic can be dis-

* Great care must be taken not to allow the gas to escape unburned into the air, and even the fumes produced by burning it should not be inhaled. It is advisable to carry on the operation under a hood.

solved out from the contents of the stomach and the solution then tested.

The compound produced in Marsh's test for arsenic is hydrogen arsenide or arseniuretted hydrogen, the formula being AsH_3, corresponding to PH_3. It cannot be made in the same way as phosphoretted hydrogen, because caustic soda does not have a similar action on arsenic as on phosphorus. It is made when the hydrogen produced by the action of an acid on zinc acts on the oxide or chloride of arsenic.

$$As_2O_3 + 12\,H = 2\,AsH_3 + 3\,H_2O.$$

The action is written in the above form with 12 H instead of 6 H_2, in order to show that the hydrogen is not regarded as formed into molecules but as acting on the arsenious anhydride in the atomic state.

It is sometimes said that the hydrogen is *nascent* or in the *nascent condition* — that is, just in the process of being formed without actually being separated. The term is not a very good one, because the outcome is the result of a number of reactions occurring together in the solution, and it often happens that a process producing hydrogen in one way causes an action to go on which will not take place when hydrogen is produced in another way. Practically all that is meant by saying that the action is due to nascent hydrogen is that when hydrogen is generated and escapes as a gas it does not act in the same way as when the substance to be acted upon is mixed with the materials which would naturally produce hydrogen. For instance, in the above case, though oxygen would be taken away from arsenic by the action of a stream of heated hydrogen, arseniuretted hydrogen would not be produced, perhaps

because at the temperature when the oxygen would be removed, arseniuretted hydrogen would be decomposed.

Arsenic pentoxide, As_2O_5, which has been already mentioned, cannot be obtained by the direct union of arsenic and oxygen, as arsenic trioxide may be. We have seen in several cases that nitric acid oxidises more readily than air or even than pure oxygen, and by the action of nitric acid on arsenic trioxide, arsenic acid is produced.

The equation is represented by the equation

$$As_2O_3 + 2\,HNO_3 + 2\,H_2O = \underset{\text{arsenic acid}}{2\,H_3AsO_4} + N_2O_3,$$

or

$$As_2O_3 + 2\,HNO_3 + 2\,H_2O = 2\,H_3AsO_4 + NO + NO_2.$$

Arsenic acid is in many respects similar to phosphoric acid H_3PO_4, but unlike the latter all the water can be driven off from it, producing As_2O_5.

Phosphoric anhydride is made by the direct union of oxygen and phosphorus, and when united with water cannot be recovered. Arsenic anhydride can only be made by first preparing its compound with water and heating.

Arsenic acid is chiefly used in calico printing, whereas arsenic trioxide is employed in the manufacture of some kinds of glass and in making some colouring matters such as Paris green, as well as for fly and rat poisons. Paris green has been largely replaced as a colouring matter by non-poisonous greens and is chiefly used as a poison for insects.

Arsenic is found native to some extent, also as sulphides, and also combined with metals. Mispickel, or arsenical pyrites, a sulphide of arsenic and iron (or pyrites in which half of the sulphur is replaced by arsenic), whose composition is represented by the formula FeAsS, is the most

common ore. When roasted it produces arsenic trioxide, which can be reduced by heating with charcoal.

Arsenic is metallic in lustre, is brittle, has a specific gravity 5.7, and has the peculiarity of subliming, that is, of going off in vapour without melting. Ice below the melting point gives off a little vapour, iodine below its melting point gives off a great deal of vapour, arsenic cannot be melted under ordinary atmospheric pressure, but the solid is converted directly into vapour. In some properties arsenic is like a metal, in some it is like a non-metal. We have seen that there are similarities between nitrogen and phosphorus and between phosphorus and arsenic. There are the compounds NH_3, PH_3, and AsH_3, but on the other hand arsenic forms alloys with metals. It makes the a ys hard and brittle and is used in the manufacture of shot in order to produce more perfectly the globular form.

Antimony. — EXPERIMENT 87. Examine a piece of metallic antimony. Is it malleable or brittle? Look at the surface or the edges, and see if it shows signs of being crystalline. Pure antimony has very distinct crystals which show on the surface in the form of a star. This is frequently used as a test of the purity of the metal. To a small piece of antimony, add strong hydrochloric acid. Does the metal apparently dissolve? Heat. Test the liquid with sulphuretted hydrogen. To another piece of antimony add strong nitric acid in the same way. What effect is produced on the metal? Filter off some of the liquid, evaporate to dryness, and see whether anything passed into solution.

Antimony forms an alloy with lead which is used as type metal. The alloy is harder than pure lead. Anti-

mony forms a compound with hydrogen, similar to the compound formed by phosphorus and arsenic. Hydrogen antimonide is very similar to hydrogen arsenide, but is still more easily decomposed.

EXPERIMENT 88. Fit up an apparatus exactly as for Marsh's test for arsenic; but, instead of adding a compound of arsenic, add some suitable compound of antimony, such as tartar emetic. Notice the appearance of the flame. The colour is slightly different from that obtained on the addition of arsenic. Examine the deposit made on a cold porcelain evaporating dish. You have now seen enough to show you that the chemist must be very careful to distinguish between arsenic and antimony. In cases of poisoning, arsenic is suspected, but the chemist must always make sure that he *proves* the presence of arsenic, and not antimony, because considerable doses of antimony compounds are sometimes used in medicine. There is a little difference in the *appearance* of the mirror produced on the porcelain dish by arsenic and antimony, and other tests can be applied to it which decide between them conclusively.

Antimony is found in nature chiefly as stibnite, a compound with sulphur, whose composition is given by the formula Sb_2S_3. The Latin name for antimony is *stibium*, whence is derived the name stibnite. It is a black, crystalline mineral, but an orange-coloured substance of the same composition is obtained by the action of sulphuretted hydrogen on a solution of an antimony compound. The metal has a specific gravity 6.7, and melts at the temperature 450° C. Phosphorus, arsenic, and antimony have a great many similarities between their compounds, and they are, in some respects, like nitrogen; but they are also like bismuth.

Bismuth. — Bismuth is a metal a good deal like antimony, being hard and brittle. It is denser than antimony, just as antimony is denser than arsenic. Its specific gravity is 9.8. It is found native and also as a sulphide, Bi_2S_3. It forms alloys, some of which are very easily melted; one called Wood's metal fuses even in boiling water.

The elements nitrogen, phosphorus, arsenic, antimony, and bismuth form a natural group, that is, they possess many similarities which make it well to set them together. Some of these similarities are such as to be taken up fully only in an advanced book on chemistry.

There are differences between the elements that are quite as interesting as their similarities. No one would think of calling nitrogen a metal, whereas bismuth has nearly all the properties of a metal. Phosphorus is also unlike a metal; antimony in many respects resembles a metal; arsenic is midway between. The higher the atomic weight, the more metallic properties do the elements of this group possess.

The compounds with hydrogen are interesting. Ammonia, NH_3, is very alkaline; phosphine, PH_3, is not appreciably alkaline, but can be made to produce salts by combining with *some* acids; arsine, AsH_3, is more readily decomposed than either ammonia or phosphine, and does not form salts, nor does stibine, SbH_3. Bismuth does not form a compound with hydrogen.

The oxygen compounds have corresponding similarities and differences. Some of the compounds of nitrogen and oxygen have neither acid nor basic properties. Some of them form acids, but none form bases. Phosphorus probably has no oxides except those which form acids. The

oxides of arsenic are acid in character, though arsenic trioxide is, in some respects, like a base ; the oxides of antimony are basic or neutral in most of their properties, though some of them act feebly as acids when treated with a strong alkali ; while the oxides of bismuth are either neutral or basic.

We have in this group, then, a very good example of how difficult it is to draw hard and fast lines in nature. No one would call oxygen and nitrogen metals ; every one would call gold, silver, iron, and copper, metals. But when we come to elements like arsenic and antimony, it is difficult to say which to call them. In some text-books of chemistry they are classed as metals, in others they are classed as non-metals. So with the distinction between acid and base. We all call sulphuric acid an acid, and lime a base ; but the oxides of arsenic and antimony behave, in some respects, like an acid oxide, in some respects like a basic oxide.

Oxides that react with sulphuric acid to produce firm compounds, we readily call basic ; oxides which react with caustic potash to produce firm compounds, we readily call acid ; but some oxides form compounds, though not very firm, with both sulphuric acid and caustic soda, and so the dividing line is not distinct. The change of properties of the elements of this group is in the order of the atomic weight, as may be seen by the following numbers : —

$$N = 14;\ P = 31;\ As = 75;\ Sb = 120;\ Bi = 207.$$

CHAPTER XIV

CARBON

Preparation of Charcoal in the Laboratory and Experiments with it. — EXPERIMENT 89. Fit up an apparatus as in the figure (Fig. 58). The test-tube *a* at the left has a delivery-tube which passes into another test-tube *b*, from which there is a delivery-tube whose end dips under water

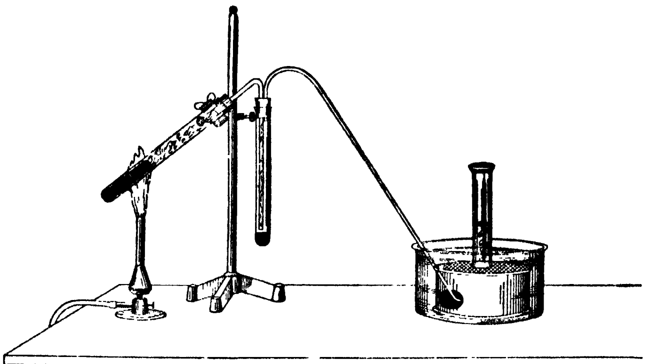


FIG. 58

in a trough so that gases may be collected. Into the tube *a* put a piece of wood, and heat. What bubbles escape at first from the delivery-tube in the trough? Why? Allow about as much gas to escape as would correspond to the volume of the test-tubes *a* and *b*, and then collect the

gas that comes over. What is the appearance of the liquid which first distils from the wood and collects in the receiver *b*? Is it more or less mobile than what distils at a higher temperature? Does more gas come over with the earlier portions of the liquid or with the later? Why does it take longer to raise the temperature of wood than to raise the temperature of iron? In order to answer this question, consider why it is impossible to heat water much above 100° C. at the ordinary atmospheric pressure. Heat the tube *a* until all action has ceased. Test some of the gas which you have collected, to see whether it is combustible or a supporter of combustion. What is the result of your test? Mix other portions of the gas in test-tubes with two, four, and eight times the volume of air, and apply a light. In which case do you get the greatest explosion?

Now examine the liquid contained in the receiver *b*. Notice the "empyreumatic" smell. Test with litmus. Is it acid, alkaline, or neutral?

As you have seen during the distillation, the liquid consists of different constituents, which may be separated from each other, though the operation is not very easily performed and is hardly suitable for you to attempt. What do you see in place of the wood? How does the volume compare with the original volume? What colour has the substance? Is it more or less easily broken than the wood from which it was made? Does it take fire more or less easily? What did you find about the combustibility of the gas obtained by heating the wood? What reason is there for the difference between the combustibility of wood and the charcoal obtained from wood?

Put a piece of the charcoal you have made, or another

piece of wood charcoal, into water. Does it sink or float? Heat to redness another piece of charcoal, holding it in the flame on the end of an iron wire or otherwise, and then dip it immediately into water. Does it sink or float? If charcoal has open spaces or pores, as you can doubtless see it has, what will fill them when the charcoal is allowed to cool in the atmosphere? Can the pores contain more air when the charcoal is hot or when it is cold? In which case will the water into which the charcoal is plunged be the better able to penetrate the pores of the charcoal? What reason is there for the different action of the hot and cold charcoal when plunged into water? Is the specific gravity of charcoal greater or less than that of water? Why is it possible for wood and charcoal to become water-logged while ice cannot be water-logged?

EXPERIMENT 90. Heat a piece of charcoal as before, and introduce it while hot into a tube containing ammonia gas over mercury, as shown in the figure (Fig. 59). Notice that though the charcoal is red hot before dipping into the mercury, it may be taken in the fingers immediately after it is under the surface of the liquid. Why is this? Is charcoal a good or a bad conductor of heat? In order to test this, hold one end of a piece of charcoal about an inch long in the fingers, and put the other end in a flame. Try a piece of iron in the same way. Which can you the more easily hold, the charcoal or the iron? Which is the better conductor of heat? What bearing has this

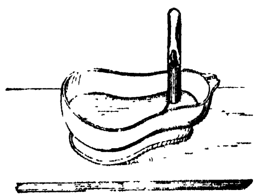


FIG. 59

experiment upon the result you obtained when putting the hot charcoal under mercury? Why does mercury rise in the tube as soon as the charcoal is introduced into the ammonia? Remove the charcoal, and once more introduce it into the flame of your burner. What difference is there between the appearance of the flame now and when the charcoal was heated in it before?

Just as charcoal absorbs ammonia, it also takes up impurities from the air, so that it is sometimes used for purifying air contaminated by sewer gas or otherwise. Bone charcoal (or bone black), obtained by the distillation of bones in the same way as wood charcoal is obtained from wood, is even more effective than wood charcoal. Bone black contains not only charcoal, but the mineral matter (chiefly calcium phosphate) contained in bones. In order to test its action, shake up water coloured with indigo or litmus with a quantity of bone charcoal, and filter. How does the colour of the filtrate compare with that of the liquid before treatment with charcoal?

Charcoal is used for clarifying sugar, oils, and other liquids, and in filters for purifying drinking water. In all cases the charcoal ultimately becomes clogged with impurities and is worse than useless for the purpose for which it is employed. It may, however, be renovated to a considerable extent by exposure to the air, and still better by reheating.

Experiment 91. Mix together powdered charcoal and powdered cupric oxide. How could water be used to separate the two after they were mixed? Heat some of the mixture in a dry test-tube, or better in a closed tube made of hard glass. What is there in cupric oxide with which carbon is ready to combine? What would be left?

What is its colour? How could you separate it from the excess of charcoal? Examine what you obtain after heating, in order to see whether your results correspond to your anticipations. If they do not, take pains to find out whether your work was faulty, or whether your anticipations were founded on wrong ideas, or were due to incorrect reasoning.

Production of Charcoal on the Large Scale. — Charcoal is made on the large scale in this country chiefly by burning wood in "charcoal pits," as shown in Fig. 60. The wood

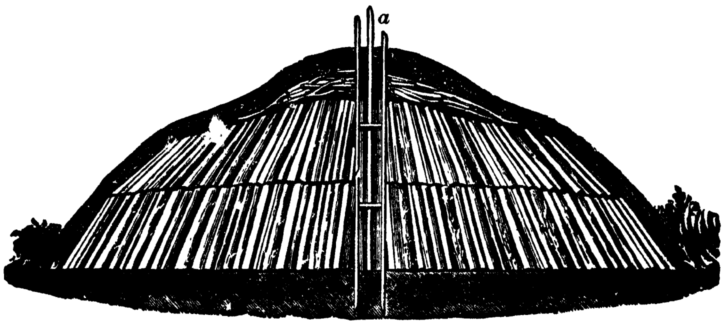


FIG. 60

is laid in piles of hemispherical shape. It is built round a central opening that serves as a chimney. The heap is covered with earth, with a few draught holes at the bottom. In this way only a small quantity of air can enter, and the combustion of the wood is incomplete. All of the volatile matters like those which you collected, are burned and thus lost, and the yield of charcoal is about 20% of the wood.* Wood is more economically carbonised

* Instead of wood being built in a heap as described, and covered with earth, it is sometimes charred in large, brick, dome-shaped enclosures.

in retorts, because in addition to the other products, about 30% of the wood is obtained as charcoal. One form of retort is shown in Fig. 61. The advantages of using the retorts is not, however, so great as might at first sight appear, because there is the expense of the retorts and fireplace, and of the fuel for heating. The gases which distil from the wood may be used for this purpose, leaving the liquid part of the distillate to be made use of otherwise. In some remote places, where wood is plentiful and the expense of retorts and other parts of the necessary plant would be large, the old method of "charcoal pits" may be preferable to what appears to be the more scientific method of distillation.

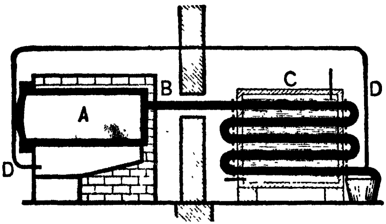


FIG. 61

Lampblack and Other Forms of Carbon. — EXPERIMENT 92. In the luminous part of a candle or gas flame, or of an oil-lamp flame, hold a piece of porcelain. What is the nature of the substance deposited on the porcelain? It is called lampblack. Lampblack is made on a large scale by the incomplete combustion of substances of an oily or resinous character, such as crude mineral oils, or the knots and other refuse from pitch-pine and hemlock. Figure 62 shows how the operation is carried out. Lampblack is used for black paint, and to a still greater extent for printer's ink.

Charcoal and lampblack are two forms of carbon, and as they are not crystalline they are called amorphous. But carbon is found in two crystallised forms, one of them

being among the softest of minerals, the other the hardest mineral known. The first is called graphite, from the Greek word which means "to write," the other is the diamond. Graphite is grayish black and of a metallic lustre, is sometimes called *black lead*, and is used in the manufacture of the so-called lead-pencils, — the very soft lead consisting chiefly of carbon, while the harder leads are mixed with other ingredients.

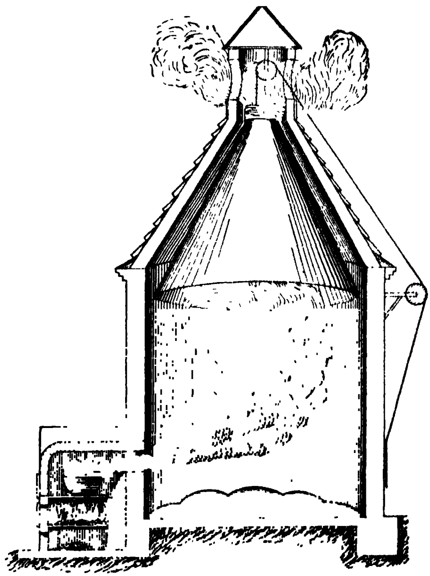


FIG. 62

Graphite is very difficult to fuse, and hence is used in the manufacture of crucibles, which are vessels such as that shown in Fig. 63, used for the melting of ores and other materials.* Graphite is also employed as a lubricant to diminish friction between rubbing metallic surfaces. It is likewise used as a protective covering for ironwork, and as stove polish. Some paints contain a large amount of graphite.

* The name crucible is said to have been given to these vessels because the old alchemists marked them with the sign of the cross in order to keep away the influence of evil spirits.

The diamond is the other crystalline form of carbon. Many diamonds are coloured, but sometimes they are perfectly clear and transparent. The coarser varieties of diamond are, because of their hardness, employed in drills for boring through rocks. Clear diamonds refract and disperse light very strongly, and therefore make very brilliant gems, having a peculiar sparkle and flash. This, with the hardness of the diamond, makes it the most valuable gem, though occasionally, on account of the fashion prevailing at the time, other gems may bring a higher price. When the diamond is heated in absence of air, it swells up and forms a black amorphous mass. Is its density thereby increased or decreased?

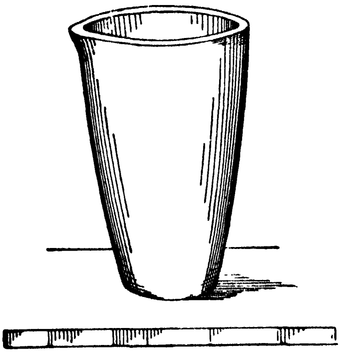


FIG. 63

What is formed when charcoal burns in air or oxygen? What is the action of the product upon lime-water? Charcoal, graphite, and diamond differ very much in appearance. How would you think it possible to show that they are merely different forms of the same element? Lavoisier, about the year 1775, was the first to prove that diamond is pure carbon.

It is easy to produce graphite or amorphous carbon from any other form of carbon, but pure brilliant diamonds have not hitherto been made, though small coloured diamonds have been produced artificially. Carbon will dissolve in molten iron just as salt dissolves in water, or

sulphur in carbon bisulphide, and if there is a good deal of carbon dissolved in the iron, part of it separates as small scales of graphite when the iron is allowed to cool slowly. Hydrochloric acid dissolves iron, but not graphite. Describe how you would separate the graphite from the iron.

It is said that if the iron is under great pressure the carbon separates in the diamond form. Possibly this is because the diamond has a greater specific gravity than graphite, and so would take less room, but we know too little about the laws of crystallisation to make any certain statement.

There is much greater difference between the specific gravity of the different forms of carbon than between those of sulphur or of phosphorus. The specific gravity of diamond is 3.3, of graphite 2.3, and of some forms of charcoal 1.6.

Coal. — You have learned that carbon is a constituent of wood. It also forms a large portion of coal. Some coals contain little else, are hard, do not soil the fingers, are difficult to light, and burn without a luminous flame. Other coals are softer, soil the fingers, are much more easily kindled, and burn with a luminous flame. The first coal is often called anthracite, the other bituminous coal; there is no distinct line between the two kinds. Compare the difference between the flame of bituminous coal and anthracite with the difference between the flame of wood and wood charcoal. What reason have you for supposing that anthracite may have been subjected to a process of destructive distillation? Does ordinary bituminous coal light more or less readily than ordinary wood? When you were distilling wood, what evidence had you that

there were various stages in the process of distillation? What reason have you for supposing that bituminous coal may have been subjected to a process similar to a partial destructive distillation?

When the rocks in which anthracite is found are examined, they show evidence of having been subjected to great pressure and heat, and thus it seems likely that the coal itself has been raised to a high temperature. From a microscopic examination of ordinary coal it appears to be formed largely from parts of plants, from the leaves and seeds and spores of trees, not very frequently from the woody stems. The partial distillation does not need very great heat if time is allowed. If the bottom of a little pool of water containing a quantity of dead leaves and plants that have lain a long time be stirred up with a stick, it will be found that bubbles of gas will rise to the surface of the water and may be lighted. This gas is somewhat similar to what you got by distilling wood. The process of decay has produced something similar to the process of distillation.

Carbon in Organic Tissue. — Not only do wood and coal contain carbon, but all animal and vegetable tissues, so that it is one of the most important elements in nature. Plants take up carbon dioxide from the air, make use of the carbon and some of the oxygen for their own tissues, and give off the rest of the oxygen into the air again. Animals feed upon plants, keep some of the carbon for their own tissues, and exhale some of it as carbon dioxide, to be again used by plants. Since carbon dioxide is produced in the body by oxygen of the air uniting with the carbon of the tissues, we have an instance of the slow burning of carbon, just as in a bog we have an

example of slow distillation. When wood decays in the presence of air, carbon dioxide is produced, and in this case also we have an example of slow combustion. It is worthy of note, however, that this slow combustion is not known to go on except in living tissues or under the influence of living organisms (the so-called bacteria of decay).

There are a number of compounds containing carbon, so many that the study of them forms a special branch of chemistry called organic chemistry. The name was given because the compounds were at one time considered to be the product of life and to be incapable of formation in any other way, but in 1828 a substance which had hitherto been obtained only from animals was formed artificially. Now, not only are many animal and vegetable products obtained artificially, but many so-called organic substances made by the chemist in the laboratory are not produced by any living organism. Though the bulk of organic compounds must be passed over, there are two or three compounds of carbon and hydrogen which it will be well to study.

Methane. — What is the formula of carbon dioxide? How many atoms of oxygen combine with one atom of carbon? How many atoms of hydrogen combine with one atom of oxygen? How many atoms of hydrogen might you, therefore, expect to combine with one atom of carbon? Is carbon dioxide a solid, a liquid, or a gas? In which of the three states might we expect the corresponding compound of carbon and hydrogen to exist?

Preparation of Methane and Experiments with the Gas. — EXPERIMENT 93. Mix together seven or eight grammes of dry sodium acetate with about three times its weight of

soda lime (a mixture of caustic soda and quicklime) and put into a hard glass test-tube, taking care that the test-tube is not more than half full. Lay the test-tube on its side, and tap it so that there will be a passage along the top for the escape of gas. Then fit up as in the figure (Fig. 64). It may be advisable to wrap wire gauze round the tube in order to make the heat, which is afterward to be applied, more uniform. Heat the tube, and after the air has been driven out collect some of the gas in cylinders, but before it ceases to come off, fit the exit tube to an apparatus such that the gas may be burned in a jet. Apply a light to the gas. What is the character of the flame? Is it luminous or non-luminous? What experiment could you try with the flame to show that the gas contains hydrogen? Suppose you invert a cylinder containing air over the flame, how could you prove that carbon dioxide is produced by the combustion? What elements do you now know to exist in the gas?

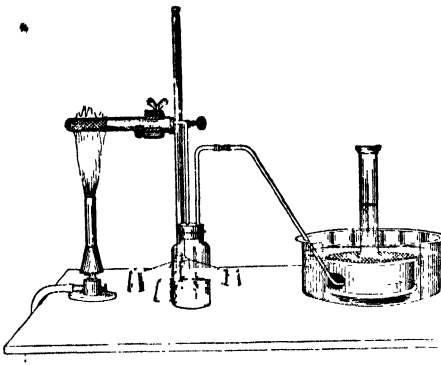


FIG. 64

It can be proved that the composition corresponds to the formula CH_4. If this is the actual formula, how many grammes of the gas would go into 22.412 litres? In this case would the gas be heavier or lighter than air?

In order to see whether the gas is in reality heavier or lighter than air, see how long it takes for a cylinder or a test-tube full of the gas to burn when the vessel is turned mouth upward and compare with the time required to burn the gas when the vessel is turned mouth downward. Introduce into a cylinder ten volumes of air with one volume of the gas and apply a light. What reason have you for considering that some portion of the air combines with great energy with the constituents of the gas? Assuming that all the carbon and hydrogen unite with oxygen of the air in the above case and that the above proportions represent the proper relative amounts of air and gas, how many volumes of pure oxygen would be required for the complete combustion of the gas? Which of the two following equations would represent the action?

$$CH_4 + 2\ O_2 = CO_2 + 2\ H_2O$$

$$C_2H_8 + 4\ O_2 = 2\ CO_2 + 4\ H_2O$$

Does the formula which you decided upon from the density of the gas correspond with that required by the volume of air needed for its complete combustion, or does it differ? What is the formula so derived?

The gas is methane, popularly called marsh gas, because found in marshes, as already described.

Its formation by the action of soda lime on sodium acetate may be represented by the equation

$$\mathbf{NaC_2H_3O_2 + NaOH = Na_2CO_3} + CH_4.$$

How many litres of methane can be prepared from eight grammes of sodium acetate?

It will be seen that the equation does not take any

account of the lime in the mixture. The reaction would go on with caustic soda alone without the presence of lime, but the latter prevents the mass from fusing too readily and attacking the glass.

How much of the carbon in sodium acetate is obtained as methane? From what does the hydrogen of the methane come? What reason is there for considering that the formula CH_3CO_2Na shows the nature of sodium acetate better than the formula $NaC_2H_3O_2$?

The reaction which goes on may be represented by writing the equation in the following form:

$$\begin{array}{r|l} CH_3 & CO_2Na \\ + \quad H & O\ Na \end{array} = CH_4 + Na_2CO_3.$$

When formulæ are written in a manner intended to show their chemical relationships, they are called structural formulæ. The formula for sodium acetate in the last equation shows the relationship supposed to exist between the two carbon atoms, one of them being united with all of the hydrogen, the other with all of the oxygen, though no particular effort is made to show the relationship existing between the latter carbon atom and the oxygen and sodium most closely connected with it.

Methane is a gas of specific gravity, 0.55, it is very slightly soluble in water, and is difficult to liquefy, requiring to be cooled to $-164°$ C. at atmospheric pressure.

In some coal mines it is found to a very considerable extent and forms a great danger because of the readiness with which a mixture with air will explode, a little more than 5% of methane being all that is required. It is called "fire-damp" by the miners, and mines in which it is found are said to be "fiery." The explosion produces

carbon dioxide, which is very suffocating and is the "choke-damp" of the miners. This forms an additional danger, because even if the direct effect of the explosion be escaped, fatal results are liable to result from the inhaling of choke damp.

ACETYLENE

Preparation of Acetylene and Experiments with the Gas. — EXPERIMENT 94. Introduce, as in Fig. 65, a small piece of calcium carbide (the size of a small bean) into a cylinder full of water inverted over a pneumatic trough. It is not a very good plan to introduce it with the fingers. The student should now be able to devise the most suitable method by which he may carry out the operation. What is the effect of the water upon the calcium carbide? When the gas ceases to be evolved, invert the cylinder, having put a cover-glass over the mouth in the usual manner; and when it is right side up, remove the cover-glass and apply a light. How does the flame of the gas compare with that of methane? Is it more or less luminous? Is the flame of methane or of this gas more like that of hydrogen?

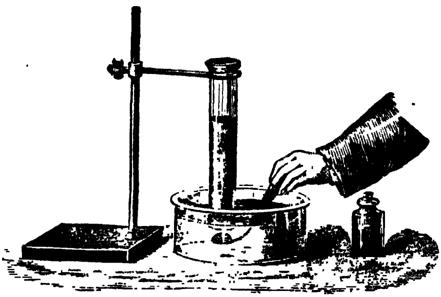


FIG. 65

The gas is acetylene.

Mix one volume of the gas with between twelve and thirteen volumes of air, and apply a light. What are

you to infer from the fact that an explosion takes place? How does it compare with the explosion of marsh gas? Be careful in trying this experiment. It is well to wrap a towel round the cylinder.

If possible, arrange some apparatus by which it will be possible to burn the gas at a jet. If you have a gas holder of the ordinary kind, it will be easy enough; if not, a bottle provided with a cork and tubes, as in the figure (Fig. 66), may be used. The tube at which the gas is to be burned has a very fine opening, smaller than is usually employed for the burning of gases; the other tube, part of which is rubber, is connected with a reservoir of water. As water flows in, the acetylene with which the bottle has been filled, and which must have no air mixed with it, flows out as a jet and may be burned. The flow of water is regulated by a pinch-cock. Figure 67 shows a simple contrivance by which the gas may be generated as required, and exhibits a special form of burner.

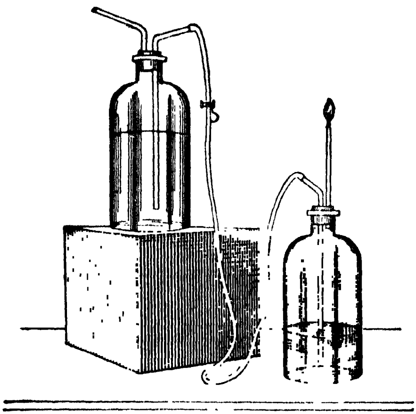


FIG. 66

Hold a dry porcelain dish just above the visible flame and see if you can obtain evidence of the existence of hydrogen in acetylene. Afterwards put the porcelain into the luminous part of the flame and see if you can obtain

evidence of the existence of carbon in the gas. What is the evidence in each case? How does the luminosity of the acetylene flame compare with a candle flame of the same size? How does the colour of the flames compare? *

Acetylene has only lately been made in large quantity, because it is only lately that calcium carbide has been manufactured upon the large scale. The carbide is prepared by heating a mixture of powdered coke and quicklime in an electric furnace.† Except at this high temperature oxygen cannot be removed from lime by means of carbon, but in the electric furnace the reaction goes on.

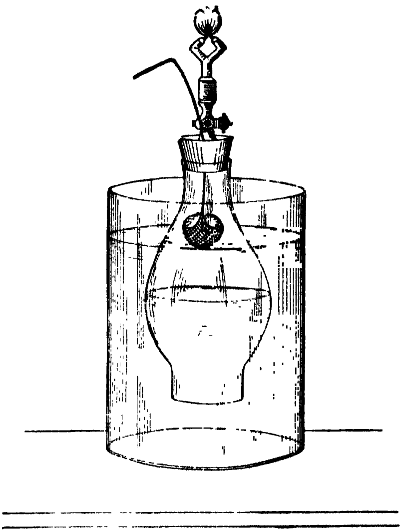


FIG. 67

$$CaO + 3\ C = CaC_2 + CO.$$

When calcium carbide is put into water the calcium once

* The acetylene flame is liable to smoke, but will not do so if the opening at which it burns is fine enough and the flow of gas is not too rapid. It is best to have a very fine opening so that considerable pressure may be put upon the gas. Special forms of burner are manufactured for the use of acetylene as an illuminant.

† Coke is the residue left by the destructive distillation of coal, and consists mainly of carbon.

more unites with oxygen, leaving hydrogen for the carbon. Why would you not expect to find quicklime produced in the reaction? What actually does happen is represented by the equation

$$CaC_2 + 2\ H_2O = CaO_2H_2 + C_2H_2.$$

What is the difference in composition between the substance represented by the formula CaO_2H_2 and quicklime?

If C_2H_2 is the formula for acetylene, how must its density compare with that of air? How could you decide by experiment whether this is approximately its density?* Assuming that C_2H_2 is the formula, make an equation representing complete combustion of the gas with oxygen. What volume of oxygen is required for the complete combustion of one litre of acetylene? What volume of carbon dioxide would be produced? How does the result of your calculation agree with what you were told about the quantity of air you were to mix with acetylene in order to obtain an explosive mixture?

The light of the acetylene flame is more like daylight than that provided by any other known illuminant, and hence colours have the same shade when illuminated by acetylene as when viewed by the light of the sun. As the flame is very brilliant, acetylene is being introduced somewhat as an illuminant instead of ordinary gas or the electric light.

Acetylene can be liquefied by a pressure of sixty-three atmospheres at 10° C., and it is sometimes sold in the liquid state in strong iron cylinders; but there have been

* Your experiment could not decide between the formula C_2H_2 and C_3H_3. That is arrived at by gravimetric analysis. The density experiment would decide between the formulæ CH, C_2H_2, C_4H_4, etc.

a number of explosions with liquid acetylene, and its use has therefore been limited. If it were not for this tendency to explode, the liquid might be used for producing gas, as it occupies a small bulk, and a cylinder of the liquid would supply light for a long time.

Ethylene is another important compound of hydrogen and carbon. Its formula is C_2H_4. At one time methane was known as light carburetted hydrogen and ethylene as heavy carburetted hydrogen. It will be seen from the formula that for the same amount of hydrogen there is twice as much carbon in ethylene as in methane. It is more dense; it is more easily liquefied, being liquefied at 0° C. under a pressure of forty-one atmospheres and at – 103° C. under ordinary atmospheric pressure. It can be made by the action of sulphuric acid on alcohol. The acid abstracts the elements of water, so that the reaction may be represented as simply a decomposition of alcohol into ethylene and water.

$$\underset{\text{alcohol}}{C_2H_6O} = \underset{\text{ethylene}}{C_2H_4} + H_2O.$$

Figure 68 shows an apparatus that may be used, but the operation is somewhat difficult. Ethylene, as might naturally be supposed from the quantity of carbon in it, burns with a luminous flame, being intermediate in this respect between methane and acetylene. Ethylene is an important part of the ordinary gas used for illuminating purposes.

Hydrocarbons — Bonds. — We have now considered three gases which are compounds of hydrogen and carbon. A large number of substances are compounds of these two elements and are called *hydrocarbons*. When there is a

considerable number of atoms of carbon in the molecule, the hydrocarbon is liquid; when there is a still larger number of carbon atoms in the molecule, the hydrocarbon is solid. You have had an illustration of this tendency in the compounds studied. Methane needs a very low temperature for its condensation, acetylene can be condensed at ordinary temperature by sufficient pressure, and ethylene is still more easily condensed.

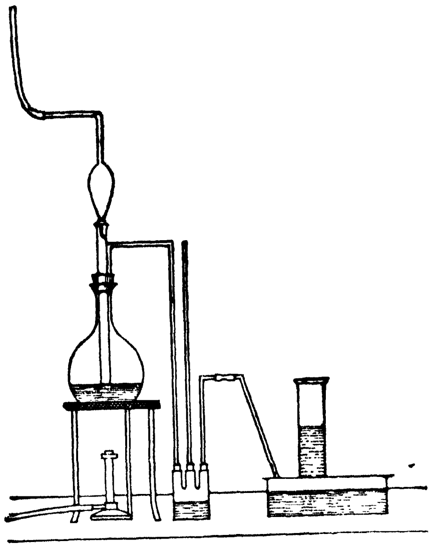


FIG. 68

In methane it is seen that one atom of carbon combines with four atoms of hydrogen, and carbon is therefore seen to be quadrivalent. We have had to deal with the compounds HCl, H_2O, NH_3, and CH_4, and we call chlorine a

univalent element, oxygen a bivalent, nitrogen a trivalent, and carbon a quadrivalent.* We do not know what physical condition is the basis of this difference between the elements. It may possibly be due to a difference of shape in the atoms, but we have no evidence upon the point. We sometimes speak of the atoms as though they were united by bonds, we say that chlorine has one bond, oxygen two, nitrogen three, and carbon four, and we represent the above formulæ in the following way:

$$\mathrm{H-Cl}, \qquad \mathrm{H-O-H}, \qquad \begin{array}{c} \\ \\ \mathrm{H-N-H}, \\ | \\ \mathrm{H} \end{array} \qquad \begin{array}{c} \mathrm{H} \\ | \\ \mathrm{H-C-H}. \\ | \\ \mathrm{H} \end{array}$$

These formulæ are not intended to represent the position of the atoms in space. $\mathrm{N}\begin{array}{l} \diagup \mathrm{H} \\ - \mathrm{H} \\ \diagdown \mathrm{H} \end{array}$ would represent the formula of ammonia as well as that given above. The giving of these formulæ does not necessarily imply that the atoms really have bonds, but their action may be represented as though they had bonds, just as we speak of a *current* of electricity, although we have no idea as to what electricity actually is.

In the compound C_2H_4 it might perhaps seem that carbon is not quadrivalent, but it is evident that if we are to represent two atoms of carbon as existing in combination in a molecule, it is as reasonable to represent them as united to each other by bonds as to represent them as

*** Monovalent and tetravalent are sometimes used instead of univalent and quadrivalent, but they are mongrel words, derived from both Greek and Latin, and therefore not so good.**

united by bonds to atoms of other elements. There is a hydrocarbon with which we have not experimented whose composition is represented by the formula C_2H_6. This formula is often written

$$\begin{array}{ccccccc} & & H & & H & & \\ & & | & & | & & \\ H & - & C & - & C & - & H \\ & & | & & | & & \\ & & H & & H & & \end{array}$$

where it will be seen that each carbon atom has four bonds. In the same way ethylene C_2H_4 may be represented by the formula

$$\begin{array}{ccc} H & & H \\ | & & | \\ C & = & C \\ | & & | \\ H & & H \end{array}$$

and acetylene by

$$\begin{array}{ccc} C & \equiv & C \\ | & & | \\ H & & H. \end{array}$$

Flame. — The gases methane, ethylene, and acetylene are constituents of most flames used for illuminating purposes, and this is a suitable place for considering flames in general. Flames always consist of a combination of gases, and all the ordinary illuminating flames consist of a combination of gases with the oxygen of the air. In the ordinary gas flame this is at once evident. In the case of lamps, the oil which is drawn up into the wick is volatilised, with more or less decomposition, and the gas so produced is what burns; in the candle the wax is first melted and afterward volatilised. Compare the combustion of charcoal and wood. In which case is there a flame? Is charcoal an easy or a difficult substance to volatilise? Though, however, burning gases produce a flame, the flame may not be luminous. Is the flame of hydrogen luminous? of carbon monoxide? of acetylene? of alcohol? of methane? Into a non-luminous flame intro-

duce a fine platinum wire or shake some powdered charcoal. Which gives the greater light, the burning gas or the solid introduced into the flame?

EXPERIMENT 95. Examine the flame of a candle.* Place a piece of porcelain in the luminous part of the flame. What evidence is there that carbon exists in the solid condition in it? At the first glance it will seem that the flame consists of two parts, — a bright yellow or luminous portion and a bluish or non-luminous portion. Examine the flame closely. Notice that there is a part of the flame near its base of a deeper blue tint than the rest. Move the candle rapidly through the air so that there is little of the luminous flame. Does the deep blue part become more or less distinct? Do you consider that the blue is more or less hot than the luminous portion? Look to see whether you can detect any flame outside the luminous part. If not, shake a dusty cloth beside the flame and see the effect, or bring a splinter of wood almost to the edge of the lower part of the luminous flame. Figure 69 represents a candle flame with its different parts differently shaded.

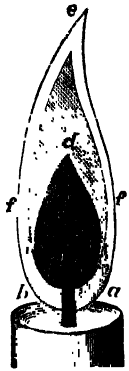


FIG. 69

Bring down over the flame, so as almost to touch the wick, a piece of stiff white paper. Remove the paper before it catches fire, but not before it is partly charred. Which part of the flame chars the paper more, the middle or the outside? See if your result corresponds with


FIG. 70

* A tallow candle with a big flame is best for these experiments.

Fig. 70. Hold across the flame a piece of wood, such as a match, until it begins to burn. Blow out the flame of the match at once, and examine the wood. There should be an uncharred portion between two charred parts. Remembering that the combustion is a combination of gases from the candle with oxygen of the air, why would you not expect the space immediately surrounding the wick to be very hot?

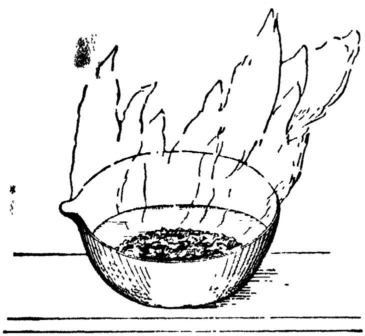


FIG. 71

A candle flame is usually described as hollow, the interior consisting merely of gas produced by a volatilisation of the melted wax of the candle. Introduce rapidly into the middle of the flame the head of a match and notice that it does not ignite for some time. If you have an alcohol lamp, make a large flame and introduce into it a small quantity of gunpowder, on the point of a knife-blade or other piece of metal. It should not catch fire. Another method of carrying out the experiment is shown in Fig. 71. Put a small heap of gunpowder upon a shallow plate or in an evaporating dish, pour a little alcohol over it and light the alcohol. Inside the burning alcohol, the gunpowder remains unaffected until the alcohol is nearly all burned off so that the outside of the flame comes in contact with the gunpowder, or until the flame is

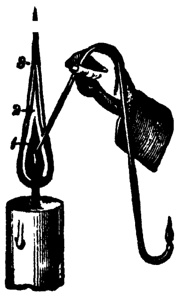


FIG. 72

blown to one side by a draught of air, which may produce the same effect. With a tube of rather fine bore you may find it possible to draw off the gases from the interior of the flame of the candle and to ignite them at the farther end of the tube in the manner shown by Fig. 72.

To illustrate the effect of cooling a flame try the following:

EXPERIMENT 96. Bring down upon the flame a sheet of metal, as in Fig. 73. How does it affect the luminosity of the flame? What reason does this experiment give you for supposing that the luminous part of the flame is hotter than the blue portions? See whether the candle can be put out by contact with the piece of metal.

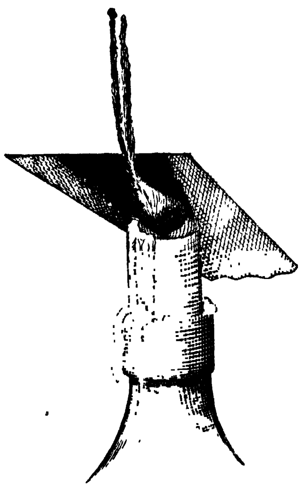


FIG. 73

Make a close spiral of half a dozen turns of fine copper wire by wrapping it round a small lead pencil or glass tube, and bring it down over the flame so that it will surround the wick, as in Fig. 74. Notice the change in luminosity of the flame before it goes out. The extinguishing of the flame is due to the gas being cooled below its kindling point by the copper wire. Hold a wire gauze over the flame, bringing it down slowly so as not to extinguish the flame. Does the flame pass through the gauze? Does the gas from the candle pass through the gauze? If it does, it should be possible to light it on the upper side of the gauze. Make the experiment.

If you have any kind of gas flame, it will be easier to perform the experiments with wire gauze. Turn on the

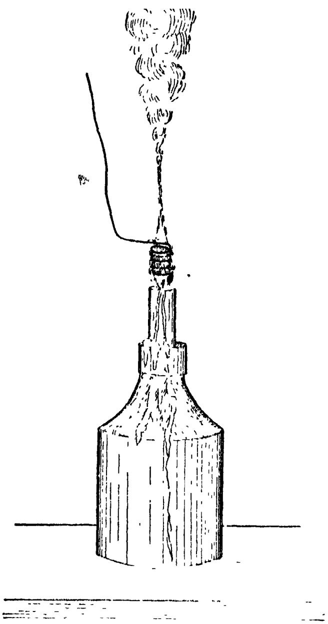


FIG. 74

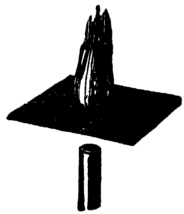


FIG. 75

gas jet without lighting the gas. Hold a piece of gauze about an inch or so above the jet, as shown in Fig. 75, apply a light above the gauze, and notice whether the gas lights below the gauze. Sir Humphry Davy, about a century ago, made use of the facts which you have noticed in order to provide protection for miners in fiery mines. His invention consists in surrounding a lamp with wire gauze and thus preventing the flame setting fire to the explosive mixture outside. Air can of course pass through the gauze, so that the lamp may be kept burning; but though the fire-damp may be seen burning inside the gauze, the gas outside does not take fire, at least for some time, so that the miner has an opportunity to leave the dangerous locality. If the gas burns a long time inside the gauze, the latter may become hot and so

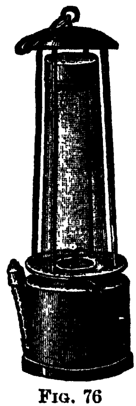


FIG. 76

set fire to the gas outside; hence Davy's "safety lamp" is useful chiefly for giving warning to the miner in time to enable him to avoid the danger. Figure 76 shows a Davy's safety lamp.

EXPERIMENT 97. If you have a supply of gas in the laboratory, make use of a Bunsen burner, named from its inventor, perhaps the most famous chemist of the nineteenth century. Figure 77 represents a Bunsen burner. Notice that the opening of the tube A from which the gas comes out is wide, in this respect quite different from the ordinary gas jet. Unscrew the upright tube and notice that the opening through which the gas issues into it is small. A Bunsen burner thus divided is represented in Fig. 78, the opening being *a*. Notice that there are two wide openings at the bottom of the upright tube. The burner is usually provided with a metal ring by which the openings may be closed. Close these openings, turn on the gas, and light it as it escapes. Can you see the parts of the flame noticed in the candle? Gradually turn the ring so as to open the holes slowly. What is the effect on the luminosity of the flame? Does the exterior non-

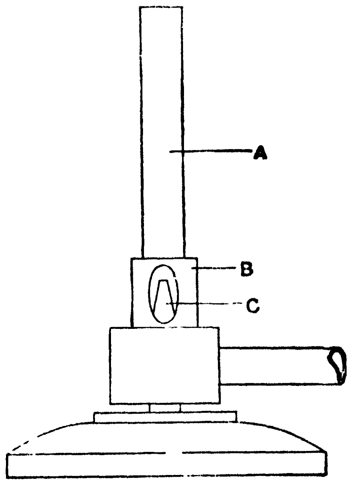


FIG. 77

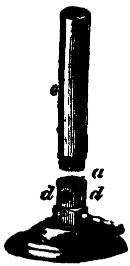


FIG. 78

luminous flame become more or less distinct? Can you still detect the four parts of the flame? Note the variations in them as the ring is turned. What do you observe about the size of the flame as a whole? Place a piece of smoking paper near the lower openings. What evidence have you that air is drawn in through these openings? When the luminous part of the flame is just disappearing, what is the colour of the inner cone? What has taken the place of the luminous part of the flame? Open the air draught as much as possible and the inner cone will probably become green; if not, turn off the gas a little. Decrease the supply of gas still more. You will probably find that the flame disappears from the top of the long tube and that the gas lights below. The flame is then said to "*strike back*." If it is allowed to remain in this condition for a minute or two, you will notice a very disagreeable smell due to acetylene, produced when gas burns with an insufficient supply of air.

In the ordinary non-luminous flame of the Bunsen burner, when the inner cone has a bluish shade, the ratio of gas to air in the mixture which reaches the top of the tube is about 1 : 2.3; when the colour is green, the ratio of gas to air is about 1 : 3.4. Suppose that the gas requires as much oxygen as would be needed for complete combustion, if it consisted of 50% methane and 50% of a gas which needs no oxygen, calculate how much air would be required and see if the ratios given above would be enough. The striking back is caused by an explosive mixture of air and gas being produced. A little consideration will make it plain that this explosive mixture contains the greatest proportion of gas to air which can explode through the tube. So long as the gas is in a greater ratio,

its mixture with air burns quietly at the top of the burner: but finally enough air mixes with the amount of gas supplied to cause a rapid ignition through the tube, the flame travelling back more quickly than the gas and air flow out.

Test which is the hottest part of the flame by seeing where a fine platinum wire placed in it becomes brightest. You should find the highest temperature at approximately the middle of the outer cone. Try experiments similar to those carried out with the candle to show the hollow nature of the ordinary non-luminous flame.

It is possible to arrange a Bunsen flame so that the inner and outer cone can be separated. Over the ordinary metal tube of the burner fit a glass tube about ten or twelve inches long, and outside this fit another glass tube of a little wider bore and arranged so that it may be moved up and down. A good way is to have between the two glass tubes one or two rubber rings (which may be made by cutting off half an inch or so of rubber tubing large enough to go over the inner glass tube). The arrangement is shown in the figure (Fig. 79). In the first instance let the outer tube project three or four inches above the inner tube and light the gas as it escapes. Diminish the supply of gas so that the proportion of air becomes greater till the inner cone finally becomes green. Diminish still further the supply of gas, and the inner cone will strike down and burn, leaving the outer cone burning at the top of the outer tube.

Modify the experiment so that the inner tube will project beyond the outer, as in Fig. 80, and light the gas. The double cone will now be seen at the top of the inner tube. Move the outer tube upwards, and it will carry with it the outer cone, leaving the inner cone burning at

the top of the inner tube. There is a possibility of the hot flame cracking the glass, so you will find it advisable to insert in the top of each glass tube a small piece of platinum foil in such a way as to form a short platinum

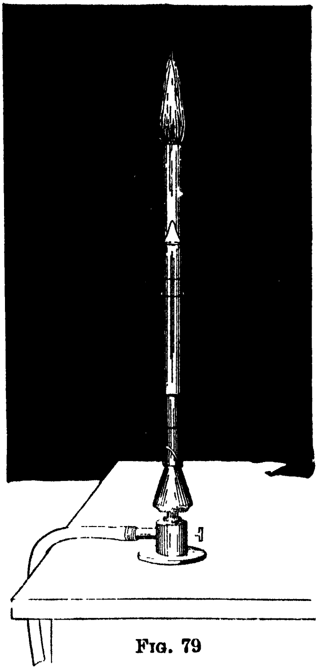


Fig. 79

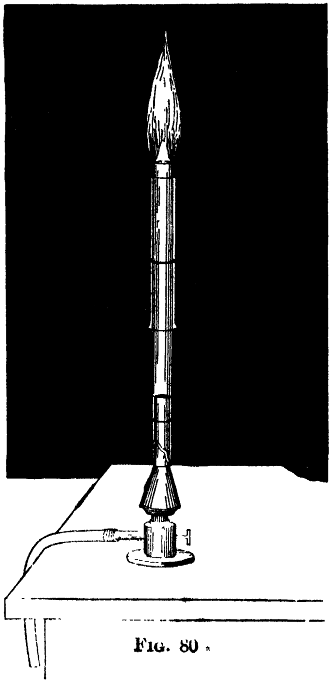


Fig. 80

tube projecting about a centimetre above the glass. See whether the upper or the lower flame is the hotter by passing a platinum wire down through them and seeing where it is brightest.

There has of late been a very extensive study of flames; the temperature of the different parts has been carefully

investigated, and the gases in different parts of the flame have been analysed. In the ordinary luminous flame there is the outer envelope, which is not easily seen, but in which the greater part of the combustion really takes place and which is the hottest part of the flame. The inner portion is partly non-luminous and partly luminous. In the non-luminous portion there is very little air and therefore a minimum of combustion; the gases are, however, heated and undergo change, the most important apparently being that some acetylene is produced. But acetylene when sufficiently heated decomposes, and by its very decomposition produces heat, for it is one of those substances which are formed only under the continuous influence of heat, and it therefore gives out heat when it decomposes.* Hence the carbon produced by the decomposition is at a high temperature and becomes luminous. The carbon takes oxygen from carbon dioxide and water vapour, which are produced in the outer envelope of the flame and which penetrate to some extent into the inner portion of the flame. Carbon monoxide and hydrogen are thus produced, and these are consumed in the outer non-luminous envelope. The deep blue part of the flame near its base is probably similar to the luminous

* Hydrogen and oxygen, when they combine to form water, give out heat, and if water is to be decomposed it requires the application of heat or some other form of energy. Water is said to be *exothermic*, because giving out heat in its formation. On the other hand, carbon and hydrogen do not readily combine to form acetylene, and some other operation by which heat is afforded must go on at the same time. In the case of the action of calcium carbide on water, the union of calcium, hydrogen and oxygen to form calcium hydroxide produces a great amount of heat and helps the union of carbon and hydrogen. Acetylene is said to be ***endothermic***, because absorbing heat in its formation.

part, except that the temperature is not high enough to cause a decomposition of the hydrocarbons into carbon and hydrogen.

The amount of air drawn in by the Bunsen burner is not sufficient for the complete combustion of the gas, and a hotter flame may be made by forcing air into the middle of the flame. This is done in the blast lamp, which consists essentially of two tubes, an inner and an outer one, as shown at *d* in Fig. 81. The inner tube supplies air, while gas is supplied through the passage between the tubes. The air is forced in through the tube, and so into the interior of the flame, by means of bellows or some similar contrivance connected with the tube *c*. The supply of air being large, the combustion of the gas is rapid and the temperature high. The blast is used in the laboratory when a high temperature is required. If oxygen be used instead of air, the temperature is still higher, because the nitrogen of the air does not support combustion and has to be heated. Hydrogen gives a higher temperature than ordinary illuminating gas, and the flame of a blast lamp in which oxygen and hydrogen are employed, and which is usually called the oxyhydrogen blowpipe, is the hottest that we can produce. Platinum, which is very difficult to melt, fuses readily in the oxyhydrogen flame, which is therefore used in the working of that metal.

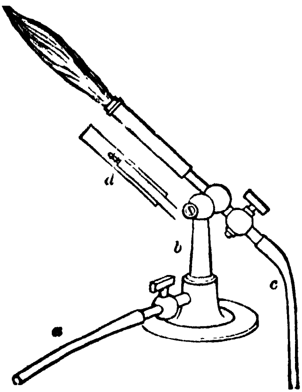


FIG. 81

The flame is non-luminous, but a solid which will not melt when put into it becomes white hot and emits light. Such a substance is quicklime, and one of the most brilliant lights known is produced by the oxyhydrogen flame striking upon a piece of quicklime. This is what is ordinarily called the lime light. (Figure 82 shows the apparatus.) Since the extensive application of electricity, the oxyhydrogen flame is not so important as it formerly was.

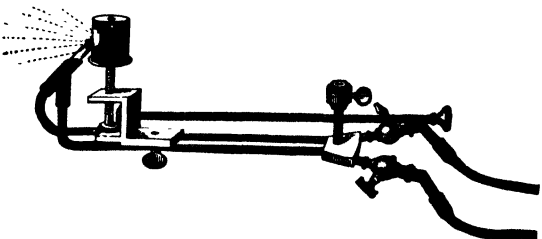


FIG. 82

Instead of a blast from a bellows, air is sometimes supplied to a small flame by means of a mouth blowpipe. The outer portion of this flame contains a quantity of heated oxygen and may be used in order to oxidise substances. For instance, a small piece of metallic arsenic placed on a stick of charcoal and heated in the outer flame is oxidised and gives arsenic trioxide. On the other hand, the interior of the flame has not sufficient oxygen for complete combustion of the gas, and so it would take oxygen from substances ready to give it. For example, if copper oxide on a stick of charcoal is submitted to the action of the inner part of the flame, oxygen is taken away and copper is left in the metallic state. The outer portion of the flame is called the oxi-

dising flame, the inner the reducing flame. The appearance of the blowpipe and the method of use is shown in the figure (Fig. 83). The mouth blowpipe is very much used for the identification of metals in ores, owing to the fact that the compounds of many metals give characteristic reactions when heated in the oxidising or reducing flames.

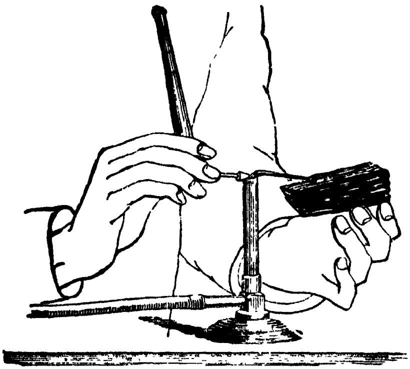


FIG. 83

Silicon and Boron. — There are two elements, silicon and boron, which are in many respects like carbon. The compound of silicon and oxygen, silica, is very common, quartz being more or less pure silica, and many rocks, such as granite, containing a large percentage of the same substance. Quartz is not acted on by ordinary acids, but hydrofluoric acid, which is in the same class as hydrochloric acid, reacts energetically with silica and its compounds, the silicates. The gas silicon fluoride is produced:

$$SiO_2 + 4\,HF = SiF_4 + 2\,H_2O.$$

Glass is a silicate, and so hydrofluoric is not kept in glass, but in wax bottles. Hydrofluoric acid is used to etch glass, the part which is not to be acted upon being protected by a coating of wax.

The compounds of boron are far less abundant than those of silicon, and neither boron nor silicon has the same interest as carbon.

CHAPTER XV

METALS

THE elements that we have so far studied have, for the most part, belonged to the class called non-metals. We saw in the group containing phosphorus, arsenic, antimony, and bismuth, that the line of division between non-metals and metals is not sharp; but it is usually convenient to make such a division. The non-metals which combine with oxygen form oxides that yield acids, and these acids may have their hydrogen replaced by a number of elements to form salts. Several of the non-metallic elements form acids simply by combining with hydrogen. Perhaps the metallic, or non-metallic, property of an element may be considered as most clearly shown by the nature of the chlorides. The chlorides of nearly all the non-metallic elements are decomposable by water. Very few of the non-metallic chlorides have been studied by us, for the very reason that they are not important and are easily decomposed. The chlorides of phosphorus (of which there are two, PCl_3 and PCl_5) are decomposed by water, and form acids. The chloride of arsenic, $AsCl_3$, also decomposes in water and forms the oxide (arsenic trioxide), unless in the presence of a large excess of hydrochloric acid. The chlorides of antimony and bismuth are partially decomposed by water, forming compounds which contain some chlorine and some oxygen. But zinc chlo-

ride, magnesium chloride, calcium chloride, potassium chloride, and sodium chloride have no tendency to decompose. The action of nitric acid is also, in many cases, an indication of the metallic, or non-metallic, character of an element. Nitric acid acting on phosphorus, arsenic, or antimony merely oxidises it, and does not form a nitrate; with bismuth a nitrate is produced which is, however, partially decomposable by water. Nitric acid also merely oxidises sulphur and carbon, but silver nitrate, cupric nitrate, cobalt nitrate, are stable salts.

Salts contain a metal and a salt radical, and if the salt radical has the opportunity to choose between two metals, it, in some cases, shows its preference in a very marked manner.

Experiment 98. Into a solution of copper sulphate put some nails, or other bright pieces of iron. What evidence do you at once have that copper is removed from the solution? Test a dilute solution of copper sulphate by adding potassium ferrocyanide solution. What appearance do you notice? Into some more of the dilute solution put a number of bright iron pieces, such as a number of tacks, and leave them until the colour of the copper sulphate disappears from the solution. Then add potassium ferrocyanide again. What kind of precipitate do you now obtain? Dissolve some iron in sulphuric acid and add potassium ferrocyanide. What kind of precipitate do you obtain? What do you infer was in the solution from which the copper had been removed by the iron? Dissolve some arsenic trioxide in hydrochloric acid, and put into the solution a strip of bright copper foil. What happens to the surface of the copper? Try the same experiment with copper in a solution of mercuric chloride.

What do you infer from the appearance of the copper in each case?

EXPERIMENT 99. Into a copper sulphate solution pour some caustic soda solution. What is the colour of the precipitate? Heat the precipitate in the liquid. What change is there in the former? Filter off and test some of the filtrate by adding hydrochloric acid and barium chloride. What have you proved to exist in the solution? The reaction on addition of the caustic soda is represented by the equation

$$CuSO_4 + 2\ NaOH = \mathbf{Cu\ (OH)_2} + Na_2SO_4,$$

and the reaction on heating is represented by

$$Cu(OH)_2 = \mathbf{CuO} + H_2O.$$

Examine a solution of ferric chloride. What colour is it? Add caustic potash solution till the liquid is alkaline to litmus. What is the appearance of the precipitate? It has much the same composition as rust. Boil the liquid together with the precipitate. Does the latter apparently change, as in the case of the precipitate obtained from the copper? Filter, and into some of the filtrate put enough hydrochloric acid to neutralise or make slightly acid, and then add potassium ferrocyanide. Is there any iron in the solution? How would you test for iron in the precipitate? Evaporate some more of the filtrate to dryness and test for potassium and for a chloride.

The reaction which takes place is represented by the equation

$$\underset{\textbf{ferric chloride}}{FeCl_3} + 3\ KOH = \underset{\textbf{ferric hydroxide}}{\mathbf{Fe\ (OH)_3}} + 3\ KCl.$$

The term "hydroxide," or "hydrate," is applied to combinations of metals with the radical OH. The hydroxides are derivatives of water, one-half of the hydrogen being replaced by the metal. A univalent metal replacing half the hydrogen in *one* molecule of water forms one molecule of an hydroxide. Thus one molecule of potassium hydroxide (or caustic potash), KOH, or of sodium hydroxide, $NaOH$, is derived from one molecule of water, HOH. On the other hand, in the formation of one molecule of cupric hydroxide, $Cu(OH)_2$, two molecules of water are required, copper in the cupric compounds being bivalent. In the case of ferric hydroxide one molecule, $Fe(OH)_3$, is derived from three molecules of water. The formula of the hydroxide may be written if the formula of the chloride is known, because for every chlorine atom in the molecule of the chloride there exists an OH group (often called *hydroxyl*) in the hydroxide. Thus, as $CaCl_2$, $MgCl_2$, $PbCl_2$, represent the molecules of the chlorides of calcium, magnesium, and lead, so $Ca(OH)_2$, $Mg(OH)_2$, $Pb(OH)_2$, represent the molecules of the hydroxides of the same metals. Sodium and potassium have a greater affinity for the radical SO_4 and the element chlorine than has either copper or iron. We found that iron has a stronger affinity for the radical SO_4 than copper has, and if a strip of iron and a strip of copper be put into a dilute solution of sulphuric acid, and joined by a wire outside the liquid, a current of electricity will flow from iron to copper in the liquid, and the iron is said to be electropositive toward copper. Sodium and potassium are electropositive toward nearly all other metals, and many metals may be obtained from their salts by the action of sodium and potassium; and though sodium and potassium as ordinarily seen do

not appear metallic, the reason is that they are so ready to combine with oxygen that the metallic lustre is seldom seen. You have already learned (page 12) how to obtain a brightly metallic surface.

Metals are, for the most part, heavy, but lithium is the lightest solid known, and there are several metals lighter than water. Most of the metals melt only at a high temperature, but mercury is liquid much below the ordinary temperature, freezing only at about $-40°$ C.

Most of the metals are of a white or grayish colour, but copper is red, while calcium, strontium, and gold are yellow. Metals are for the most part good conductors of electricity, though the variation in this respect is considerable.

The combinations which metals make with each other differ from those which they make with non-metals. In the first place, they combine, in most cases, in all proportions, and moreover the combinations are rather mixtures than compounds, being something like solutions, though alloys are sometimes obtained in crystals in which the elements are in atomic proportions. Alloys do not lose their metallic appearance, and their properties are more nearly a mean of the properties of the constituents than is the case with more decided chemical compounds.

In the chemical study of metals the combinations with non-metals are most important, and we found it impossible to study the non-metals without at the same time learning some of the properties of metals.

CHAPTER XVI

THE ALKALI METALS

Sodium. — One of the most common substances is common salt. You have already learned that it is composed of sodium and chlorine. Nearly all of the compounds of sodium are made by taking it as the starting point. The largest chemical industry is connected with the treatment of common salt for the products to be obtained from it, so much so that the name "chemical works" is applied to works in which salt is one of the raw materials.

Salt is obtained from sea-water, from rock salt, and from salt brines derived from springs, lakes, or wells. In hot countries salt is obtained from sea-water by evaporation; in cold countries the salt solution is concentrated by freezing, because, as you saw at the very beginning of your work, ice formed from salt water contains very little salt, and hence the solution left behind contains a larger proportion of salt than the original sea-water.

Rock salt is occasionally found pure enough for use, grinding only being necessary; more frequently it must be purified. Brines from salt wells contain a larger proportion of salt than sea-water, and hence do not need so much fuel for evaporation.

From common salt by the action of strong sulphuric acid, sodium sulphate is made, hydrochloric acid being produced at the same time. The operation is carried on

in large furnaces, in one form of which the floor is circular and rotates; the mixed sodium chloride and sulphuric acid are introduced in a continuous stream to the middle of the rotating "hearth," and are gradually worked by mechanical scrapers towards the edge. By this time the hydrochloric acid has been all driven off, and the sodium sulphate is ready to be removed from the hearth The sulphate is called "saltcake," and is mainly used for the manufacture of soda. Some is, however, employed in glass making, in the production of ultramarine, and to some extent in medicine.

When sodium sulphate is dissolved in water and allowed to crystallise by evaporating the solution at the ordinary temperature, the crystals have the composition represented by the formula Na_2SO_4, 10 H_2O, and constitute "Glauber's salts," the form used in medicine.

When this crystallised sodium sulphate is dissolved in water, it is found that the solubility increases with the temperature up to about 33° C., after which it decreases. It is also found that if a solution is evaporated between the temperatures 33° C. and 40° C., the sulphate deposited contains no water of crystallisation. Hence the solubility below 33° C. is the solubility of the hydrated salt, Na_2SO_4, 10 H_2O; while the solubility above 33° C. is the solubility of the anhydrous salt, Na_2SO_4. The solubility of anhydrous sodium sulphate decreases with rise of temperature, and thus the increase of solubility followed by the decrease is accounted for.

EXPERIMENT 100. — Mix in a beaker powdered crystalline sodium sulphate, Na_2SO_4, 10 H_2O, with strong hydrochloric acid, both being at the temperature of the laboratory. What evidence does the outside of the beaker

in a short time give that the mixture is cold? In the liquid formed, allow a test-tube containing water to remain for some time. What happens to the water? Test the temperature with a thermometer. What temperature do you find? Sodium chloride, which is formed in the reaction, does not contain water of crystallisation. What becomes of the water? What effect does that have upon the temperature?

By far the greatest quantity of sodium sulphate made is used in the manufacture of sodium carbonate in "soda" works. The process employed was invented by Le Blanc, who won the prize offered by the French Academy for the best method of preparation of sodium carbonate from common salt. Le Blanc's process was patented in 1791, but in the French Revolution his property was seized and he committed suicide. The process has been but slightly changed to the present day. Sodium chloride cannot be changed into carbonate by the action of carbonic acid, because the latter is a weak acid, and so a roundabout process is employed. Sodium chloride is first changed to sodium sulphate. It seems at first sight that the goal is no nearer, because sodium sulphate is just as little acted upon by carbonic acid as sodium chloride is. But when sodium sulphate is heated with a mixture of coal dust and calcium carbonate (limestone), it is reduced to sodium sulphide, which at the high temperature (1000° C.) reacts on the limestone. The process may be represented by the following equations:

$$2\ \mathbf{NaCl} + H_2SO_4 = \mathbf{Na_2SO_4} + 2\ \mathit{HCl}$$

$$\mathbf{Na_2SO_4} + 2\ \mathbf{C} = \mathbf{Na_2S} + 2\ \mathit{CO_2}$$

$$\mathbf{Na_2S} + \mathbf{CaCO_3} = \mathbf{CaS} + \mathbf{Na_2CO_3}$$

The product is called black ash, and contains about 45% of sodium carbonate. A small excess of coal gives a black or dark gray colour.

The mass is "lixiviated," or treated with a small quantity of water, the sodium carbonate is dissolved, the calcium sulphide being left undissolved.

The sodium carbonate solution when evaporated forms crystals of the formula $Na_2CO_3, 10\,H_2O$. We saw that when crystals of ice are formed in salt water the ice contains very little salt. In the same way, when crystals of a salt such as sodium carbonate are formed, the impurities are for the most part excluded. Hence, when a substance contains impurities from which it is desired to free it, a common method is to dissolve it in water and allow it to crystallise. What proportion of water is there in the soda crystals? When the carbonate is to be sent to a distance, it is often more economical to use fuel to drive off the water than to pay freight on it. Sodium carbonate is called washing soda, because used for laundry purposes. The dry salt is employed in making glass and was formerly used in the preparation of metallic sodium, while from the solution, caustic soda is prepared.

Another process for making sodium carbonate is the Solvay or ammonia soda process. This process depends upon the fact that the acid sodium carbonate $NaHCO_3$ is only sparingly soluble in a cold solution of sodium chloride containing ammonia. So when ammonia is added to common salt solution, and carbon dioxide passed into the mixture, the reaction goes on as represented by the equation

$$NaCl + NH_3 + H_2O + CO_2 = NaHCO_3 + NH_4Cl.$$

The sodium acid carbonate separates out in crystalline form. On being heated it loses water and half of the carbon dioxide, as shown below:

$$2\ NaHCO_3 = Na_2CO_3 + H_2O + CO_2.$$

The carbon dioxide set free is used with another quantity of salt and ammonia. The ammonia can be recovered from the ammonium chloride by heating with lime, and the lime is obtained from the limestone which supplies the carbon dioxide. It will be seen from the following equations how the action goes:

$$CaCO_3 = CaO + CO_2$$

$$2\ NaCl + 2\ NH_3 + 2\ H_2O + 2\ CO_2 = 2\ NaHCO_3 + 2\ NH_4Cl$$

$$2\ NaHCO_3 = Na_2CO_3 + CO_2 + H_2O$$

$$2\ NH_4Cl + CaO = CaCl_2 + 2\ NH_3 + H_2O$$

In considering these equations it must be remembered that an equation represents the obtaining of a certain definite amount of various substances from a given definite amount of other substances. How many molecules of ammonium chloride are represented as formed in the second equation? How many are used in the fourth? What is represented as being made from the ammonium chloride in the fourth equation? What substances are represented on the left-hand side of these equations which do not appear on the right? What substances are represented on the right hand of the equations that do not appear on the left? The substances on the left-hand side are the raw materials; those on the right-hand side are the products obtained.

Suppose we consider the matter without reference to

equations. What is it that the manufacturer wishes to obtain for the purposes of sale? From what does the metallic part of this compound come? From what does the salt radical part come? It is evident that since matter cannot be made from nothing, the metal and the salt radical must be supplied by the raw materials to the same extent, at least, as they are made use of in the compound wanted. If supplied in larger amount, it would follow that so far as the process under consideration is concerned there would be a loss. Now the raw material supplying the metallic part and the raw material supplying the salt radical part both have other constituents, and these must form one or more products. It will be seen on consideration that calcium chloride is the other product obtained. If calcium chloride were needed to the same extent as sodium carbonate, the process would be exceptionally satisfactory, but unfortunately calcium chloride is practically a waste product, and the useful result of the whole action is that sodium carbonate is obtained.

In the Le Blanc process it will be seen that sodium chloride is constantly supplied, just as in the ammonia soda process; but, besides this, sulphuric acid, coal, and limestone are also required. It will be seen that the same amount of limestone is necessary as in the ammonia soda process, because in both cases all of the carbon dioxide comes from the limestone. In both processes sodium chloride supplies the metallic part of the sodium carbonate and limestone supplies the salt radical. The carbon of the coal in reducing sodium sulphate produces carbon dioxide, but it is not available for making sodium carbonate, and is lost. The sulphur of the sulphuric acid ultimately appears in calcium sulphide, which, as such, is

not only valueless, but even a nuisance, because when exposed to the air it yields sulphuretted hydrogen. Many efforts have been made to recover the sulphur in order to regenerate sulphuric acid, and partially successful methods have been invented, but the sulphuric acid is not all recovered.

Further observation of the equations shows that hydrochloric acid is one of the products. This acid was at first allowed to go to waste, escaping into the air; but as its existence in the atmosphere was very obnoxious, manufacturers were forbidden by law to allow its escape. It was then employed for the manufacture of chlorine used in making bleaching powder; and for many years the Le Blanc process has been able to make a stand against the ammonia soda process only because the latter does not provide a convenient method for the manufacture of this important product. The ammonia soda process was made practical by Solvay, a Belgian, in the year 1863, and entered into competition with the Le Blanc process, which had been in use for seventy years; and now half of the world's supply of sodium carbonate is made in this way.

Sulphuric acid is needed in the Le Blanc process, and it is made on the premises. In the manufacture of sulphuric acid nitric acid is required, and it is also made on the premises. As already stated, bleaching powder is also produced, and hence a soda, or, as it is often called, an alkali, works is very extensive.

Caustic soda is manufactured from sodium carbonate by the action of "milk of lime," that is, lime suspended in water.

The reaction is represented by the equation

$$Na_2CO_3 + Ca(OH)_2 = CaCO_3 + 2\ NaOH.$$

The calcium carbonate produced is a solid and is allowed to settle, while the caustic soda solution is drawn off into cast-iron kettles, the water evaporated, and the caustic soda fused.

Lately electrolytic methods have been used for obtaining caustic soda. Common salt solution is electrolysed; chlorine passes off at the positive pole; and the sodium set free acts on water, producing caustic soda. The action may be represented by the equations

$$NaCl = Na + \mathit{Cl}$$

$$Na + H_2O = NaOH + \mathit{H}$$

Are these equations molecular? Could they be used in exactly the sa· · way as our ordinary equations to calculate the *volumes* of the gases set free?

State in words the action of chlorine on caustic soda that is represented by the following equation:

$$2\ NaOH + \mathit{Cl}_2 = NaOCl + NaCl + H_2O.$$

It is one of the difficulties in the electrolytic process for making caustic soda that chlorine and caustic soda are liable to mix. There are various ways of preventing the mixing, but they are expensive. It seems still a little doubtful whether electrolytic methods will entirely replace the other methods, but nearly all the improvements now made are in the electrolytic methods. The electrolytic method requires as raw material only common salt solution, and both the products, caustic soda and chlorine, are very valuable; but the apparatus required is costly, and the action of the chlorine on it is very destructive.

EXPERIMENT 101. Dissolve some sodium carbonate, say twenty grammes, in twice its weight of water, put into a beaker, and pass into it a stream of carbon dioxide. A good way of carrying out the operation is to have the delivery-tube of the carbon dioxide apparatus attached to a funnel which dips into the carbonate solution, as shown in the figure (Fig. 84). What weight of crystallised carbonate (the hydrated salt, washing soda crystals) would be equivalent to the twenty grammes of dry carbonate? What evidence is there that carbon dioxide is absorbed by sodium carbonate? If it is not plain that this is so, devise some method of deciding whether it is or not. The compound produced is sodium hydrogen carbonate, more frequently called sodium acid carbonate, or bicarbonate of soda. The formula is $NaHCO_3$. Why should it be called bicarbonate? The most common name of all is baking soda.

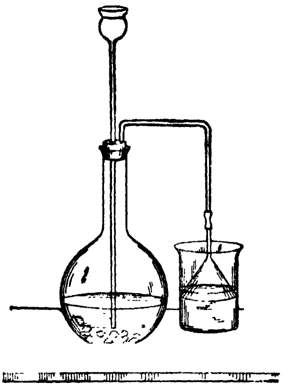


FIG. 84

Make an equation representing the formation of sodium bicarbonate by the action of carbon dioxide on an aqueous solution of sodium carbonate. Is sodium acid carbonate more or less soluble than sodium normal carbonate? What reason can you give for your opinion? Why was it suggested that you should use a funnel in the beaker rather than the ordinary delivery-tube?

Until 1807 the compound nature of caustic soda, though suspected by chemists, was not proved, but in that year Sir

Humphry Davy decomposed it by a current of electricity, and thus obtained metallic sodium. The process was very expensive, however, and another method was afterward discovered, namely, that of heating sodium carbonate with charcoal. This process was employed for a long time, but in 1887 was replaced by a process invented by Castner, which consists in heating caustic soda with carbon. The carbon, if introduced in the form of charcoal, would float on the surface of the fused caustic soda, and thus not act properly; hence it is combined or intimately mixed with iron. The temperature required is much lower than when sodium carbonate is heated with charcoal. The reaction is represented by the equation

$$3\ NaOH + C = Na_2CO_3 + 3\ H + Na.$$

How much of the sodium in the caustic soda is obtained in the metallic form? Why is the rest of it not necessarily lost? This new process enabled sodium to be made more cheaply, the price falling from \$1.25 to \$0.75 a pound. This was of great importance, because sodium was used in the manufacture of aluminium, which at that time came prominently into notice. In 1889 Castner succeeded in producing sodium still more cheaply by the electrolysis of fused caustic soda. At the present time nearly all of the sodium of commerce is made in that way, so that there is, to a certain extent, a return to the original method by which sodium was obtained. Electrical power is much cheaper than in Davy's time, and details of the process have been modified. In the works where Castner's process was first applied it is possible to turn out nearly a ton of sodium every day. The price of sodium was reduced to \$0.50 a pound. But aluminium is not now made by the

action of sodium, but by an electrical process, hence other uses had to be found for sodium, or its production must be largely curtailed. At the present time one of the most important uses of sodium is in making sodium peroxide, which is employed for bleaching purposes, being more convenient to handle than peroxide of hydrogen, which can only be preserved in aqueous solution, and is therefore more bulky. From sodium peroxide hydrogen peroxide can be made whenever it is required.

Potassium. — Potassium is a metal very like sodium. It was first prepared by Davy in 1807, by the electrolysis of caustic potash. Caustic potash and caustic soda are so much alike that naturally when he succeeded in decomposing one of them and so obtaining the metal, he tried to decompose the other. Potassium was the first to be obtained; afterwards sodium was prepared in the same manner.

In one of your early experiments you found which of these metals acts most readily on water. If you have forgotten, throw a very small piece of each metal into water, and observe the result. Are potassium and sodium lighter or heavier than water? The specific gravity of potassium is only about eight-ninths that of sodium.

EXPERIMENT 102. Melt some paraffin wax in a dry test-tube by putting the test-tube into boiling water. When the paraffin is melted, put into it a small piece of potassium. Into another test-tube with paraffin, in the same way, put a piece of sodium. Which melts easier, potassium or sodium? An alloy of the two in the proper proportions is liquid at the ordinary temperature.

Potassium is much more difficult to prepare than sodium, largely because its chemical reactions are more energetic.

It is therefore much more expensive, and so there is a much greater difference between the price of the metals potassium and sodium than between the price of caustic potash and caustic soda.

Potassium compounds were formerly made chiefly from potassium carbonate, obtained by lixiviating wood ashes; hence the name potash. In Russia and America wood is even yet burned to a small extent for the sake of obtaining potash, but at the present time by far the greater quantity of potassium salts is made from potassium chloride procured from the salt mines of Stassfurt in Germany, the process being essentially the same as for the sodium salts.

EXPERIMENT 103. Allow a piece of caustic soda and of caustic potash to stand for a few minutes in the air. Which of them has taken up the more water from the air? Expose potassium carbonate and sodium carbonate to the air for an hour or so. If the air is *damp*, one of them will have taken up enough water to appear quite moist, while the other will not appear to have absorbed moisture. Which of the two, sodium carbonate and potassium carbonate, is "*deliquescent*"? Potassium nitrate does not take up moisture from the air so readily as sodium nitrate. Give one reason why potassium nitrate is used in gunpowder instead of sodium nitrate.

Whether a salt of potassium or of sodium will be used for a given purpose very often depends upon which is more easily obtained pure, a statement that usually means, which salt will crystallise the easier; and it is seldom that the same salts of sodium and of potassium are used extensively. For instance, potassium cyanide, ferrocyanide, iodide, and permanganate are more common

and important than the corresponding sodium salts, whereas sodium sulphate, sulphite, phosphate, and acetate are more used commercially than the corresponding potassium salts. In a few cases the difference between the compounds of the two metals is such that both are used. Caustic potash acting upon fats produces soft soap, while caustic soda under the same conditions produces hard soap. Glass is a silicate, usually of lime, with either potash or soda; potash glass is hard and difficult to fuse; soda glass is softer and more fusible. Silica, used in making glass, is obtained from pure sand; soda is supplied either in the form of carbonate or of sulphate; the former fuses more easily, but the latter is cheaper. Potash is supplied as carbonate, very rarely as sulphate, for the latter does not act well. Lime is obtained from chalk or limestone.

Ammonium. — When ammonia combines with an acid, a substance is produced very similar to the salt produced by the action of the same acid upon caustic potash. When caustic potash is added to hydrochloric acid, potassium chloride is obtained, water being at the same time produced. Ammonia and hydrochloric acid combine to form a salt very similar to potassium chloride, and to it the name ammonium chloride is given. In the same way ammonium sulphate and ammonium nitrate correspond to potassium sulphate and potassium nitrate. The substance ammonium has never been prepared, but the group of the elements nitrogen and hydrogen represented by the formula NH_4 passes from one compound to another. Just as potassium chloride when acted on by sulphuric acid yields potassium sulphate, so ammonium chloride acted on by sulphuric acid yields ammonium sulphate.

Though ammonium itself has not been obtained, an alloy of it with mercury (ammonium amalgam) is not difficult to prepare, though it is difficult to preserve.

EXPERIMENT 104. Into a dry test-tube put a few grammes of mercury, then introduce a small piece (half the size of a pea) of sodium, cork the test-tube very loosely, and heat gently. There should be a flash of light when the mercury is sufficiently heated, the sodium forming an alloy with the mercury. Hence care should be taken in the operation. Introduce another small piece of sodium, and if necessary again heat, repeating the process till the mercury is seen to become solid; then remove from the test-tube (perhaps you may need to break the test-tube). Why were you told to cork the test-tube *loosel* ? The substance produced is sodium amalgam. What action does it have on water? What are the substances produced? Why does the solid change to a liquid? What is the reaction toward litmus of the water after the amalgam is put into it? If your previous knowledge does not enable you to answer these questions, make the experiments with a small portion of the amalgam that you have prepared. Then into a strong solution of ammonium chloride in a porcelain dish put another small portion of your amalgam. What change do you notice in the amalgam? How does it appear as compared with what is obtained by the action of the amalgam on water alone? Describe the feeling to the fingers of the substance. The substance that you are examining is called ammonium amalgam. Allow it to stand for a few minutes. What change takes place in it? What are the bubbles that are coming off? In order to determine this point, put the main portion of the

sodium amalgam into a test-tube, fill three-fourths of the tube with concentrated ammonium chloride solution, and after the amalgam has expanded fill the test-tube to the top with water, invert over a vessel of water, and collect the gas as in Fig. 85. Test it with a lighted match.

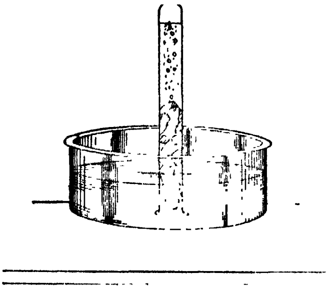


FIG. 85

Lithium, Rubidium, Cæsium. — These three metals belong to the same group as sodium and potassium, lithium being less active, and rubidium and cæsium being more active. The last two are on this account very difficult indeed to prepare, and as the salts even are rare, the metals are very expensive. Cæsium is the most energetic of all the metals.

CHAPTER XVII

THE METALS OF THE ALKALINE EARTHS

EXPERIMENT 105. Place in separate watch-glasses, or in other convenient dishes, small quantities of calcium chloride, strontium chloride, and barium chloride. Test each of them on a platinum wire in the flame. Which substances are most similar in the colour of their flame?

Pour about 2 c.c. strong sulphuric acid into a test-tube, upon a little calcium chloride (about as much as an apple seed — better in the form of powder than in a lump). What substances will be produced by the action of the sulphuric acid on the chloride?

Complete the equation

$$CaCl_2 + H_2SO_4 =$$

Carefully heat the test-tube till the sulphuric acid begins to fume, unless the solid has previously dissolved. Would hot sulphuric acid or hot water give the worse burn? What conclusion do you come to as to whether calcium sulphate is soluble in strong sulphuric acid? After the sulphuric acid is cold, pour it into about 200 c.c. of water. Notice whether or not a precipitate is formed.

Repeat the experiment, using strontium chloride and barium chloride instead of calcium chloride. Which sulphate of the three is apparently the most readily soluble in water? Which sulphate is least soluble?

By this time you will probably notice that one of the chlorides in the watch-glass has deliquesced considerably. Which one is it? Allow the glasses to stand open to the air for several days. Which ones now exhibit deliquescence?

The most important salts of barium are barium sulphate, used in the arts as a pigment instead of white lead, and barium chloride, employed in the laboratory as a test for sulphuric acid and sulphates. The most commonly used salt of strontium is the nitrate employed for making coloured lights (red fire). The compounds of calcium are by far the most important.

EXPERIMENT 106. Upon a piece of calcite (or if calcite is not convenient, upon a piece of marble) put dilute hydrochloric acid. What do you observe? Hold in the gas produced a drop of lime-water on the end of a glass rod. What is the gas? Wrap one end of a platinum wire round a small fragment of calcite (half the size of an apple seed) and hold the calcite for two or three minutes in a Bunsen burner flame just above the green inner cone. What change do you see in the lump of calcite? Put the substance into a dish, and allow a drop of water to fall upon it. What happens? Add a few more drops of water, and test the substance with litmus-paper. How does this substance differ from calcite in respect to its action with litmus? What reason have you for considering that by your treatment of calcite you have obtained a substance similar to caustic soda? How could you prove that calcite contains something which is also in calcium chloride?

The operation which you have performed on the very small scale in heating calcite is carried out on the large

scale in lime kilns. Limestone is strongly heated, and *quick*lime is produced, which, when acted on by water, gives *slaked* lime. Place a lump of good quicklime on a porcelain plate or evaporating dish, and pour over it a little less than its own volume of water. What evidence have you of energetic chemical action? What change is there in the consistency of the substance? The reaction is represented by the equation

$$CaO + H_2O = Ca(OH)_2.$$

Lime is mainly used in plaster and mortar for building purposes, but also in the purification of coal gas, in the tanning of leather, and in many other operations.

EXPERIMENT 107. Shake up some slaked lime with water. How would you show that though slaked lime is not *very* soluble, it is soluble to a slight extent. Slaked lime in suspension in water is "milk of lime"; the solution separate from the solid sediment is "lime-water."

Pass through clean lime-water a current of carbon dioxide. The cloudiness first produced is due to calcium carbonate, which is practically insoluble in water. Pass the carbon dioxide still longer till the precipitate dissolves. Did we find in a former experiment that *sodium* bicarbonate is more or less soluble than *sodium* carbonate? What conclusion do you now draw regarding *calcium* bicarbonate as compared with *calcium* carbonate? Mix about equal volumes of bicarbonate solution and of the original lime-water. Why do you get a precipitate? Filter off the precipitate. Does the filtrate contain as much lime as an equal volume of bicarbonate solution?

Make a solution of soap, add a little to the water containing calcium bicarbonate (bicarbonate of lime), and

shake. The appearance produced is that caused by hard water. Add some soap solution in the same way to the filtrate mentioned above, and you should find it easier to produce a lather. The water has been made less hard. In limestone districts the water, especially in wells, is hard, because the limestone (calcium carbonate) dissolves in the water of the soil which always contains carbon dioxide. Such water may be softened by adding lime-water, and allowing the precipitate formed to settle; so that we have, what at first seems strange, the fact that water which is hard because it contains a compound of lime may sometimes be made soft by adding lime.

Heat some of the bicarbonate solution. What evidence have you that the bicarbonate is decomposed by heat? Why should water in some cases be softened by boiling? Water is sometimes hard because containing calcium sulphate; such water is not softened by either of the above methods which are effectual with bicarbonate, and is said to have *permanent* hardness, while the hardness due to bicarbonate is *temporary*.

EXPERIMENT 108. Heat some gypsum in a test-tube. What is driven off from it? If the gypsum is in the form of a transparent crystal (selenite) notice the change in appearance. Heat some powdered gypsum for five or ten minutes in a porcelain dish, keeping the flame moving under it, so that it will not become very hot in any part. The temperature should not rise above 200° C., and 125° C. is best. Mix the powder so obtained with about one-third its weight of water, and allow to stand. You should find that the powder takes up water, and hardens or sets into a solid mass. You have made "plaster of Paris." Heat another portion of gypsum to a red heat.

How does the substance obtained act with water? In the first case you drove out approximately three-fourths of the water from the gypsum; in the second case you drove out all of the water. The mineral anhydrite is calcium sulphate without water. Why can it not be used for making plaster of Paris?

A very important compound of calcium is bleaching powder, obtained by passing chlorine over slaked lime. The name chloride of lime has been given to it. The precise nature of the compound, in other words its constitution, is not thoroughly understood; but when dissolved in water it forms calcium chloride and calcium hypochlorite, and the latter, or the hypochlorous acid or chlorine produced from it, is what bleaches. Exactly what is produced depends upon the treatment to which the chloride of lime is subjected.

Calcium, strontium, and barium produce hydrates which are alkaline like those of potassium and sodium, and, on the other hand, they form compounds having a character which we call earthy, and hence the metals are called metals of the alkaline earths.

Compounds of calcium, strontium, and barium frequently crystallise in the same form, or are *isomorphous*, and in many cases the compounds of lead are isomorphous with them. In some respects lead is similar to the alkaline earths, but it is more closely allied to tin.

CHAPTER XVIII

THE ZINC GROUP OF METALS

THERE is another group of elements somewhat connected with those just considered. They are for the most part bivalent, so that the formulæ of their compounds are written in the same manner. The metals are magnesium, zinc, cadmium, and mercury. Magnesium carbonate and to a certain extent the other carbonates, when they exist, are similar to those of calcium, strontium, and barium. But the sulphates are for the most part very soluble, unlike those of the alkaline earths, and the metals themselves are much more easily prepared than those of the previous group. The properties of the metals have a very noticeable gradation. They do not act on water at the ordinary temperature, but magnesium and zinc both act on water vapour at a high temperature, magnesium more readily than zinc. Magnesium is the hardest and cadmium the softest of the three solid metals. The specific gravity goes in the order, magnesium, zinc, cadmium, and mercury. On the other hand, the fusibility and volatility are in the exact reverse order, mercury being a liquid at the ordinary temperature, while magnesium requires quite a high temperature to melt it. Magnesium has a considerable affinity for oxygen, and when heated burns very brilliantly in air, the light being used for photographic purposes. Zinc does not oxidise quite so

readily, but it also burns brilliantly, especially if heated in pure oxygen. Cadmium oxidises at a high temperature in the air, but not so easily as the other elements. Mercury oxidises perceptibly if kept at a temperature 250° C.–300° C. for several days, but the oxide decomposes at a slightly higher temperature.

The relative tendency to combine with oxygen is seen in the minerals containing the elements. Magnesium is found as carbonate either alone or with calcium carbonate, also as sulphate (Epsom salts), as silicate in talc (French chalk), asbestos, and meerschaum, but not as sulphide. Zinc is also found as carbonate and silicate, but the most important ore is the sulphide (zinc blende). Cadmium is frequently found in small quantity in zinc ores, chiefly blende, but the only pure mineral known is the sulphide. Mercury is mainly found as sulphide (cinnabar), also in the metallic form, but not combined with oxygen. The metallurgy of the metals illustrates the relative affinities for oxygen. When cinnabar is roasted, the oxygen of the air combines with the sulphur and the mercury volatilises. Cadmium and zinc sulphides are roasted to change them to oxide, and the oxide is heated with charcoal. Magnesium oxide cannot be reduced in this way. The method used till lately was to heat the chloride with sodium, the reaction following the course indicated by the equation

$$MgCl_2 + 2\ Na = Mg + 2\ NaCl.$$

The method used by Bunsen and now largely employed, is to electrolyse the double chloride of magnesium and potassium, the magnesium being set free more easily than the potassium. Though minerals containing magnesium are the most common and are the cheapest, the metal itself

is by far the most expensive, costing more than ten times as much as zinc. Mercury and cadmium are more expensive than zinc, the ores being less common, but they cost little more than half as much as magnesium.

The salts of magnesium, while being bitter, are not in the ordinary sense poisonous; those of zinc are nauseating; while the salts of mercury, having a similar composition, are violent poisons when taken inwardly. Mercuric chloride (corrosive sublimate) has a very poisonous action upon microbes. Some microbes by their growth cause suppuration in a wound or in any part cut open by a surgeon. Mercuric chloride has a very poisonous action upon these microbes, and a solution dilute enough not to hurt the tissues of the body, but strong enough to kill the microbes, is used for washing out wounds, healing being thus promoted.

The gradation of properties which we have noticed corresponds with a gradation in the atomic weights. Magnesium has the lowest atomic weight, then zinc, afterward cadmium, and finally mercury. There is a similar gradation in many of the properties of the alkaline earth metals. What is the order of the solubilities of the sulphates of calcium, barium, and strontium?

Mercury has some properties distinctly differing from those of the other metals of the group. It forms two classes of compounds, — the *mercuric* salts, which are in many respects similar to those of magnesium, zinc, and cadmium, and the *mercurous* salts, which have no analogies among the salts of the other metals. In the mercuric salts mercury acts as a bivalent element; in the mercurous salts the compounds are such as would be formed by a monovalent element. Mercurous chloride has the formula

HgCl, while that of mercuric chloride is $HgCl_2$. Mercurous chloride is insoluble in water, in this respect resembling silver chloride.

Magnesium has a number of uses, but the most important is as an illuminant for flash lights and similar purposes. Zinc is employed as a coating for iron goods, so-called "galvanised iron" being sheet-iron coated with zinc to prevent rusting. It is a constituent of brass and of German silver. Mercury is largely used in the extraction of gold and silver from their ores, forming with these metals an amalgam from which the mercury is afterward volatilised and recovered. Many amalgams are useful, some being employed for filling teeth and some in making mirrors. Pure mercury is used in thermometers and barometers. Cadmium is the least useful of the four metals.

CHAPTER XIX

THE IRON GROUP OF METALS

Iron. — Iron is the most important of the metals, about forty million tons a year being smelted, one-third of it in the United States. Iron is sometimes found native, but not in sufficient quantity to be more than a curiosity, being mainly of meteoric origin. In compounds it is very widely distributed, the reddish tint in weathered rocks being due to iron in a form similar to that of rust. But iron compounds must contain the iron in large quantity, and in a form easy to extract before they can be economically used as *ores* of iron. The most important ores are the oxides and the carbonates. There are two important oxides, — magnetite, which when pure contains 72.4 % of iron, being represented by the formula Fe_3O_4, and hematite, containing 70 %, its formula being Fe_2O_3. Magnetite is nearly black, is brittle, heavy, and magnetic. Hematite is non-magnetic, in general reddish, and for the most part not quite so heavy as magnetite. Limonite, sometimes called brown hematite, contains water as well as the oxide found in hematite. It is not so heavy as hematite, and has a yellowish colour when scratched, thus being distinguished from hematite, which is red when scratched. Siderite is ferrous carbonate, $FeCO_3$, containing when pure 48.27 % of iron. Clay iron stone contains clay mixed with siderite, and in *black band* siderite is

mixed with carbonaceous material, in some cases to such an extent that little fuel is necessary in the reduction of the metal.

The ores of iron usually contain impurities, such as silica and silicates, and these must be removed. The most important method for reducing iron from its ores is that of the blast furnace. The blast furnace is built of a specially infusible brick, to which the name fire-brick is given. Its shape is that of a double cone, the lower cone being the shorter, as shown in the figure (Fig. 86). It is sometimes eighty to a hundred feet in height, and fifteen or twenty feet in greatest width. The fuel (coke, coal, or charcoal) is introduced at the top, together with the iron ore and the material which is to remove the impurities. The most important of the *fluxes* added is limestone, since it combines with silica, and forms a fusible *slag*, leaving the iron comparatively pure. The air to support the combustion is sent as a *blast* into the lower part of the furnace, just above the place where the molten metal and slag are to be collected. The blast enters through tuyeres (pronounced *tweers*), which are iron pipes, whose number differs in different furnaces, and whose size also varies. The air is heated before being sent into the furnace, so that the temperature of the furnace may be kept higher than would be possible with a cold blast. The reactions that take place in the furnace are complicated, but consist essentially in the change of carbon dioxide into carbon monoxide by contact with carbon, and of carbon monoxide into carbon dioxide by the action of the iron oxides. The carbon dioxide is in the first place produced by the burning of the fuel in excess of air, and by the heating of the limestone. As the iron ore gives up

its oxygen to the fuel it is reduced to metallic iron, which combines with a certain quantity of carbon, and also with a small amount of silicon and other substances, reduced at the same time from the impurities present. The

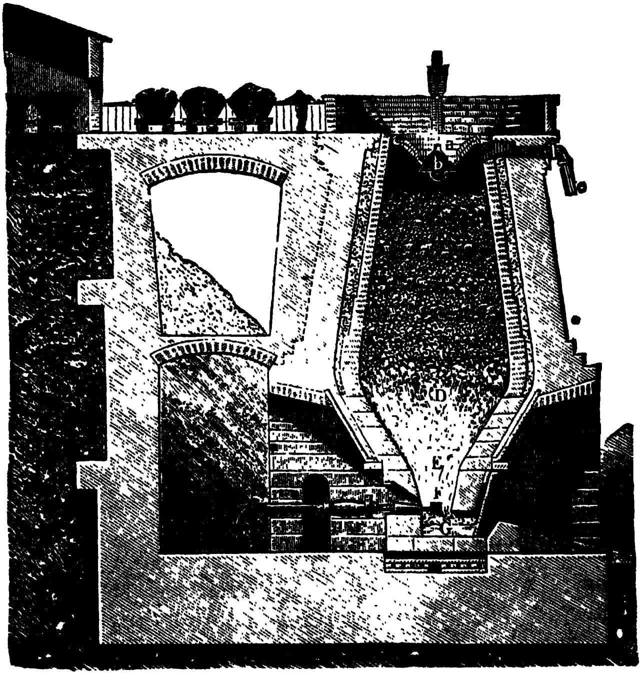


FIG. 86

greater part of the impurities combines with the lime of the limestone and produces the slag, a molten mass which is not so heavy as molten iron, and collects on the top of it. There are thus at the bottom of the furnace two molten layers, — iron beneath and slag above. Every

few hours these two layers are run off from the furnace through *tap holes*, which are at other times kept plugged with clay.

The iron is run into moulds, usually made of sand,* and is thus shaped into bars or *pigs*. This is *cast-iron*, and contains carbon and silicon, with occasionally phosphorus and sulphur. The carbon in pig-iron sometimes amounts to as much as $4\frac{1}{2}$ %. It may be either combined with the iron or diffused through it in crystalline scales. When the carbon is mainly combined the iron is *white;* when it is mainly free the iron is *gray;* when partly combined and partly free the iron is *mottled*. Iron cooled rapidly is white, because rapid cooling does not give time for the separation of crystals. White iron is harder than gray iron.

It is in general true that alloys melt at a lower temperature than pure metals, and cast-iron melts more readily than pure iron. Moreover, when it solidifies it expands somewhat, and is therefore suitable for making casts taking the form of the mould. In making a casting the metal is melted, and run into a mould of the required form. Cast-iron is more brittle than pure iron, and cannot be hammered or beaten into shape as the latter can. This purer iron, *wrought-iron*, is made from pig-iron by melt-

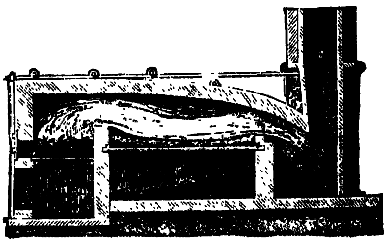


FIG. 87

* In large works the iron is sometimes run into large receptacles, where it is kept liquid till ready for conversion into steel.

ing the latter and heating it in such a manner that the impurities are oxidised and removed. The process is carried out in a *puddling* furnace, the shape of which is shown in the figure (Fig. 87). The fuel is in a grate, separated from the metal, which is melted by the hot flame reflected from the roof of the hearth upon the iron. Owing to its form the furnace is called a *reverberatory furnace*. Along with the gases from the grate, hot air strikes upon the pig-iron and oxidises the impurities, which are removed in the slag. As the iron becomes purified it melts less easily, and becomes pasty.

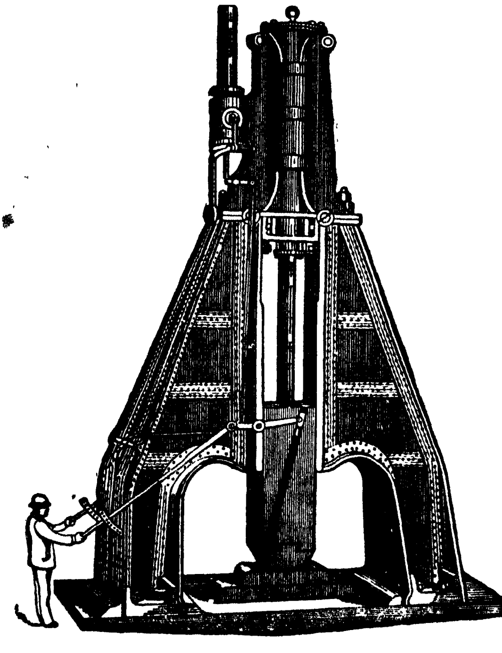


Fig. 88

When the impurities are nearly all oxidised the iron is removed in lumps, and hammered or squeezed to press out the slag and weld the mass together. A form of hammer is shown in Fig. 88. Wrought-iron is fibrous in its structure, is ductile, malleable, tough, and soft. It cannot

be hardened by rapid cooling. Two pieces of wrought-iron, heated to a pasty condition, may be *welded* by pressure or hammering, thus forming one piece.

Steel contains less carbon than cast-iron, and more than wrought-iron. Other substances, such as nickel and manganese, are sometimes added to it. The properties of

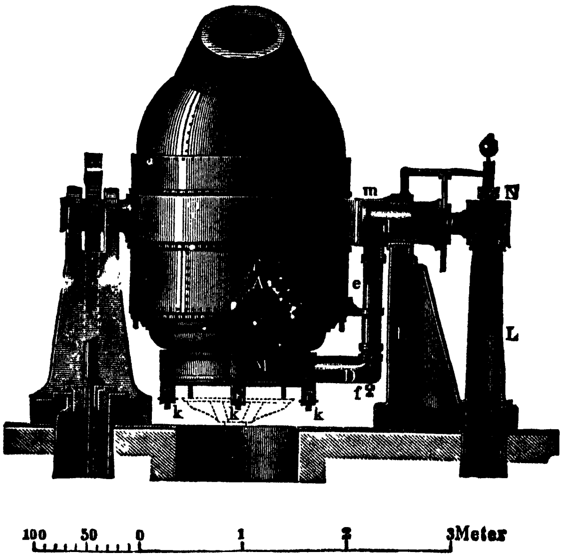


FIG. 89

steel depend partly upon the nature and quantity of the substances contained in it, and partly upon the manner of tempering. Ordinary steel contains from 0.15 % to 1.8 % of carbon. It was formerly made from wrought-iron, by heating it in a bed of charcoal for a fortnight or longer. Steel made by this method is expensive, and now nearly all of the steel manufactured is produced by the

Bessemer process. This process consists in blowing air through a quantity of molten cast-iron in a "converter" of the shape shown in the figure (Fig. 89). When the carbon is practically all removed a certain quantity of *spiegeleisen*, an alloy of iron containing a considerable amount of carbon and manganese, is added, so as to introduce the proper quantity of carbon. The presence of manganese is advantageous. Sometimes carborundum, a compound of carbon and silicon, is added.

Steel is in general finely granular in structure, not having the fibrous character of wrought-iron, though if broken by a slow-acting stress it has a somewhat fibrous appearance. Steel when suddenly cooled by dipping it into a liquid, such as water or oil, becomes very hard, and the hardened steel is *tempered* by heating carefully to a temperature between 220° C. and 316° C. The higher the temperature to which the steel is heated in tempering the softer it becomes, because at the higher temperature the particles of the steel become more readily rearranged.

Iron forms two classes of compounds, — the ferrous and ferric. Which compounds have the greater proportion of iron? Ferrous chloride has the formula $FeCl_2$ and ferric chloride the formula $FeCl_3$; the corresponding oxides are FeO and Fe_2O_3. In order to illustrate the difference, perform the following:

EXPERIMENT 109. Dissolve some iron tacks in dilute sulphuric acid, filter the solution, and divide the filtrate into several parts. To the first add caustic soda solution. What is the colour of the precipitate? It is almost entirely ferrous hydrate, but slightly oxidised by the oxygen of the air.

$$FeSO_4 + 2\,NaOH = Na_2SO_4 + Fe(OH)_2.$$

To another portion of the solution add slowly a solution of potassium permanganate. Notice whether the permanganate colours the solution at first, and, if not, whether it is possible to add enough permanganate to give a colour.

To a third portion of the solution add a few drops of nitric acid. What change takes place in the solution? Heat gently. Divide this solution into two parts and add to one of them caustic soda. How does the precipitate compare in appearance with that obtained before? To the second portion add a few drops of potassium permanganate. What effect is produced by the permanganate? Nitric acid is an oxidising agent, and in the presence of excess of sulphuric acid changes ferrous sulphate into ferric sulphate, in which caustic soda produces ferric hydrate.

$$Fe_2(SO_4)_3 + 6\ NaOH = 3\ Na_2SO_4 + 2\ \mathbf{Fe(OH)_3}.$$

Potassium permanganate is also an oxidising agent, and when added to the acid ferrous sulphate solution gives up its oxygen, forming a colourless solution, and it is only when all of the iron is changed to the ferric condition that the violet colour of the permanganate is seen. But when the iron has been all oxidised by nitric acid or otherwise, the permanganate is not required to oxidise it, and the violet colour appears on the addition of a few drops.

Nickel and Cobalt.—Nickel and cobalt are in many respects like iron, but they are not so common nor so important. Nickel is found in an oxidised form as silicate, but the most important ore contains it as a sulphide along with iron, often mixed with a copper ore. The sulphide is less easily oxidised than iron sulphide, and along with copper sulphide is separated from iron by oxidising

the latter and removing it in a slag. The nickel is afterward separated from the copper. Nickel, when heated in a current of carbon monoxide to a temperature of 50° C., forms a gaseous compound $Ni(CO)_4$, which decomposes at 180° C., yielding pure nickel. This property has lately been used as a method of preparing pure nickel.

Nickel does not oxidise so readily as iron, and is used as a plating to keep iron and steel from rusting. A small percentage of nickel renders steel very hard and tough and specially suitable for the armour of warships. Another advantage is that the alloy of iron with nickel is less affected by changes of temperature; therefore ships and other heavy structures are less strained when nickel steel is used in their construction. Cobalt is commercially not so important as nickel. Both metals are magnetic, but not so magnetic as iron.

Manganese. — Manganese is also somewhat similar to iron, though its compounds are for the most part different. The metal itself is not largely used, but when added to steel makes it very hard. Manganese forms some oxides that are acid in character, and one of the most important compounds of manganese is potassium permanganate $KMnO_4$, a powerful oxidising agent used as a disinfectant, also in bleaching and dyeing and in medicine.

Aluminium. — Aluminium is a chief constituent of clay, one of the most common minerals. The metal is very difficult to extract from its ores, because aluminium has such a strong affinity for oxygen. Hence, though aluminium was first separated in 1827, it was for sixty years little more than a curiosity. It was not found possible, as in the case of iron, to remove oxygen from the oxide by means of carbon in the ordinary furnace, and the

method employed for preparing the metal was heating aluminium chloride with sodium. Now, however, in the electrical furnace, the oxide, usually in the presence of molten cryolite (a double fluoride of sodium and aluminium), is reduced and metallic aluminium obtained. It is a white metal and very light, having a specific gravity 2.6. It is very ductile and malleable and a good conductor of electricity. So it is in some respects a substitute for iron and in some for copper. It is used largely as an electric conductor, also for the vibrating parts of machinery, and is replacing lithographic stone. Its uses are becoming more and more numerous and will increase with every diminution of price.

One of the most important compounds of aluminium is alum K_2SO_4, $Al_2(SO_4)_3$, 24 H_2O. It is extensively used in dye works as a *mordant*, that is, as a substance to fix the colouring matter in cloth. Aluminium sulphate, "paper-makers' alum," is now largely replacing ordinary alum in industrial processes.

Chromium. — Chromium is an element in some respects like aluminium, forming compounds similar to ordinary alum. These compounds are used as mordants and in tanning. The most important salt is potassium dichromate, $K_2Cr_2O_7$, an oxidising agent used in making coal tar dyes, in bleaching, in dyeing, and in the preparation of leather. Other compounds are used as pigments, for example, chrome yellow, $PbCrO_4$. Chromium in the metallic state is used in making steel.

CHAPTER XX

METALS OF THE LEAD AND OF THE COPPER GROUP

Lead and Tin

Lead. — Lead is a metal with a bluish tinge. It is soft, being easily cut with a knife. It is heavier than iron, its specific gravity being 11.3, but it is far from being the heaviest metal, notwithstanding the phrase "heavy as lead." The heavier metals are, however, not so common, gold, for instance, being seldom seen in large quantity. Lead melts easily, and the metal can be readily hammered and bent. It is therefore useful for making water pipes and is largely employed in plumbing.

There are two important oxides of lead. One of them, litharge, whose composition is shown by the formula PbO, is employed in the preparation of boiled linseed oil and also in the making of lead glass. In lead glass, lead oxide is used instead of lime; the glass is heavy and very brilliant, and is used in *cut* glass. Red lead, or minium, Pb_3O_4, is more valuable for making lead glass, because the excess of oxygen is useful in getting rid of impurities in the materials. Red lead is also a valuable pigment. By far the most important pigment is white lead, a mixture of carbonate and hydroxide of lead. The best quality is made by a slow process. Many attempts have been made to invent a more rapid process and so to produce the white lead at lower cost. The difficulty with

the white lead made by most, if not all, of the rapid methods, is that it is not so opaque and has not so good a covering power as that made by the older and slower process. Many substances, such as zinc white (an oxide of zinc), and barytes (barium sulphate), have been put upon the market, but they are inferior in these respects to white lead, which is, however, open to the objection that it is poisonous.

Lead is chiefly obtained from the sulphide galena, commonly found as a deposit in limestone. The sulphur is burned off, the process being somewhat complicated, because oxygen not only removes part of the sulphur, but also oxidises some of the lead to oxide, while some of the lead sulphide is changed to sulphate. At the end of the process, however, metallic lead is obtained. Galena very frequently contains silver, and the greater part of the silver in the market is obtained from *argentiferous* (silver-bearing) galena. The silver is obtained with the lead. One process of separating silver from lead is to melt the argentiferous lead and allow it to cool. Nearly pure lead crystallises out just as nearly pure ice is formed when salt water is frozen, and the solid lead is removed, leaving a lead very rich in silver. When this lead is heated in air it oxidises, forming the oxide litharge. The operation is carried on in a *cupel*, a dish made of bone-ash. The litharge is partly volatilised and is partly absorbed by the cupel. The silver does not oxidise, and so is left pure. It is difficult to entirely free lead from silver, and hence perfectly pure lead is more expensive than lead containing a small amount of silver.

Tin. — Tin belongs to the same group of elements as lead. It is a white metal and does not tarnish readily in

the air. It is therefore used as a covering for iron, tin plate being sheet iron covered with a coating of tin. A bar of tin when bent gives a peculiar sound, called the "tin-cry," due to friction of the crystals upon each other. Tin forms useful alloys; gun metal and bronze are alloys of copper and tin, and tin amalgam is used for coating the backs of mirrors. The only important ore of tin is tinstone, the dioxide SnO_2. The oxygen is readily removed by heating the ore with anthracite.

$$SnO_2 + 2\,C = Sn + 2\,CO.$$

Various salts of tin are valuable mordants.

Copper, Silver, Gold

Copper, silver, and gold are metals which have some similarities and form a group. They all form compounds in which they act as univalent elements; for instance, there are the chlorides CuCl, AgCl, and AuCl. But the more common chloride of copper has the formula $CuCl_2$, and of gold the formula $AuCl_3$.

Copper. — Copper is the most easily oxidised of the three metals, being oxidised by heating in the air; silver and gold cannot be oxidised directly by oxygen, and the oxides when produced are easily decomposed by heat alone.

Experiment 110. Into a test-tube (preferably of hard glass) put a mixture of copper oxide and charcoal powder and fit up as shown in Fig. 90. Heat and pass the gas into lime-water.

Copper oxide readily gives up oxygen when heated with carbon, carbon dioxide and copper being produced.

$$2\,CuO + C = 2\,Cu + CO_2.$$

An oxide such as zinc oxide or tin oxide, which is less readily reduced, requires a higher temperature, and carbon monoxide is produced instead of carbon dioxide.

$$ZnO + C = Zn + CO.$$

All three metals — copper, silver, and gold — are found native, but copper is also found as a sulphide, frequently with iron, as in copper pyrites $CuFeS_2$. Silver is also found as sulphide, mainly in galena. Gold occurs almost always in the metallic state, containing, however, other metals alloyed with it The extraction of copper from copper pyrites depends upon the fact that iron is more easily oxidised than copper, which holds more firmly to the sulphur. The pyrites is roasted and the roasted mass is heated with silica, which combines with the oxide of iron, forming a slag and allowing the copper sulphide to collect. Finally, the copper sulphide is oxidised by roasting, thus removing the sulphur and leaving the copper.

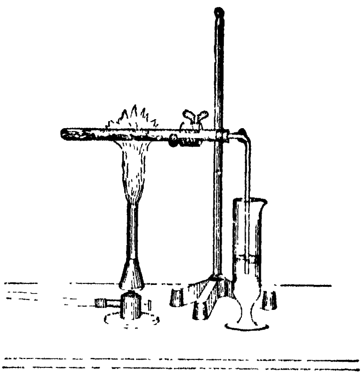


FIG. 90

$$CuS + O_2 = 2\,Cu + SO_2.$$

The copper is in a somewhat impure state. Copper is used for electrical purposes, being a very good conductor, nearly as good as silver, which is, of course, too expensive to be employed in this way. Slight impurities in copper

diminish its conductivity very much, and hence very pure copper is necessary. Nearly all of the pure copper of commerce is now obtained by electrolysis. An impure copper is arranged to form the positive pole or anode, in a solution of copper sulphate, and when the current of electricity is passed through the solution, pure copper is deposited on the negative pole or cathode. The copper of the positive pole goes into solution and the impurities are left behind.

Copper is a red metal; it is soft and tough, malleable and ductile. Its alloys with tin have been already mentioned; with zinc it forms brass.

Silver. — The method by which silver is obtained from argentiferous galena has been already described. Silver is a white metal, mainly used for coinage, for tableware such as forks and spoons, and for jewellery. The principal use of silver salts is in photography. Many silver salts are affected by the light. If to a solution of silver nitrate a chloride is added, silver chloride is produced as a white, curdy precipitate, but on standing for some time in the light it becomes dark. Many silver salts are affected by light, and ordinary photographic plates contain compounds which are very sensitive. Light produces an effect on the plate, which, however, cannot be detected till the plate is *developed*. In the process of developing, the silver compounds in the part of the plate which has been exposed to a strong light are darkened and rendered insoluble in certain liquids that dissolve the unaffected silver salts, while the parts of the plate less exposed are less darkened. In this way the lights and shades of the object photographed are reproduced and a likeness is obtained.

Gold. — Gold is found in the gravel of some streams, and is separated by washing away the lighter material, leaving the gold. It is also found in quartz veins, from which it is usually extracted by crushing the ore and bringing it into contact with mercury, which forms an amalgam with the gold, from which the mercury is afterwards driven off by heat. The gold is usually not all extracted by this method, and a process of extraction suitable for poor ores is by the use of potassium cyanide. The reaction is not perfectly understood. Some investigators claim that the presence of oxygen is necessary and give the equation

$$4\,\mathbf{Au} + 8\,KCN + 2\,H_2O + O_2 = 4\,KAu(CN)_2 + 4\,KOH.$$

Other experimenters contend that oxygen is not necessary. In any case a double cyanide of potassium and gold is formed, from which gold is obtained usually by replacement by zinc. Instead of potassium cyanide alone, a mixture of potassium and sodium cyanides may be used. This mixture is made by the action of metallic sodium on potassium ferrocyanide, $K_4Fe(CN)_6$. Thus another use for metallic sodium is provided. Gold is one of the heaviest metals. It is the most malleable of metals and can be beaten into sheets so thin as to be transparent, being very much thinner than the thinnest tissue paper. Though the metal is yellow, light shows greenish through the thin sheets. Gold is valuable chiefly because it does not tarnish, and the supply is so limited that its possession indicates wealth. Because its value fluctuates so little, it is the standard medium of exchange, and paper and silver money have their value because they represent a certain amount of gold.

APPENDIX A

THE THERMOMETER

THE thermometer is a measurer of temperature. The only kind necessary to describe here is the mercury thermometer, in which temperature is measured by the expansion of mercury.

A capillary tube, together with a bulb blown at one end, is filled with mercury at such a temperature that when cooled it will fill the bulb and a small piece of the stem. The tube is then closed.

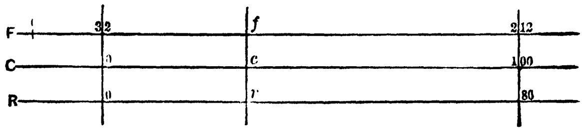
In order to graduate the tube, the thermometer is placed in melting ice, the position of the mercury marked, the thermometer being then placed in the vapour of boiling water, and the position of the mercury again marked. These two fixed points enable the thermometer to be graduated.

There are two thermometric scales in which the melting point of ice is taken as the zero. These are the Centigrade and Réaumur scales. In the former the boiling point of water is called 100 (whence the name centigrade); in the latter, 80.

In the Fahrenheit scale the distance between the melting point of ice and the boiling point of water is divided into 180 parts. The melting of ice is, however, not the zero, but is called 32°, and the zero probably marks what Fahrenheit considered the lowest *attainable* temperature.

The method of changing from one scale to the other is so clearly given in Tait's "Heat" that I transcribe it. "If we suppose the same thermometer to have these three separate scales adjusted to it or (still better) engraved side by side

upon the tube, we easily see how to reduce from one scale to the other.



"For if f, c, r be the various readings of one temperature, it is obvious that

$f-32$ bears the same ratio	to $(212-32$ or$)$	180
that c bears	to	100
and r bears	to	80

"Hence
$$\frac{f-32}{180}=\frac{c}{100}=\frac{r}{80}."$$

APPENDIX B

THE LAW OF RECIPROCAL PROPORTIONS OR RECIPROCAL RATIOS

THE law of reciprocal proportions goes with the law of definite proportions and the law of multiple proportions, and, like them, is a statement of the results of experiment.

It may be stated thus: If one element unites with a second in the ratio of a to b and with a third in the ratio of a to c, then the second and third elements will unite in the ratio of b to c or of some simple multiple of b to some simple multiple of c.

For example, 100 parts by weight, such as ounces or grammes, of oxygen unite with 1293 parts by weight of lead, and 100 parts by weight of oxygen unite with 443 parts by weight of chlorine. It has been found, by analysis of lead chloride, that 1293 parts by weight of lead unite with 443 parts by weight of chlorine.

Again: 100 parts by weight of hydrogen unite with 793 parts by weight of oxygen and with 300 parts by weight of carbon. There are two important compounds of oxygen and carbon, in one of which 793 parts of oxygen unite with 300 parts of carbon, and in the other 793 parts of oxygen unite with twice 300 parts of carbon.

It will be noticed that we started out with 100 parts by weight of *oxygen* as the standard in one instance and with 100 parts by weight of *hydrogen* as standard in the other. In the same way any element might be made the standard. Instead

of saying that 100 parts of oxygen unite with 1293 parts of lead and with 443 parts of chlorine, we might say 100 parts of lead unite with 7.74 parts of oxygen and with 34.26 parts of chlorine, and the ratios between lead and oxygen, lead and chlorine, and oxygen and chlorine, would be the same as before.

Since the law of reciprocal proportions holds, it is possible to obtain a series of numbers that represent the ratios in which all the different elements enter into combination. These numbers are arrived at by analysis of compounds of the elements or by synthesis; that is, by building up the compounds from the elements.

For instance, 100 parts by weight of oxygen unite with 1293 parts of lead; 1293 of lead unite with 443 of chlorine; 443 of chlorine with 288 of sodium; 288 of sodium with 1000 of bromine; 1000 of bromine with 489 of potassium; 489 of potassium with 1587 of iodine; 1587 of iodine with 12.6 of hydrogen.

We have thus a table of numbers for the different elements:

Oxygen	100
Lead	1293
Chlorine	443
Sodium	288
Bromine	1000
Potassium	489
Iodine	1587
Hydrogen	12.6

These numbers or simple multiples of them are the ratios in which the different elements unite.

Lead unites with bromine in the ratio of 1293 to 1000; potassium unites with oxygen in the ratio of 489 to 100; hydrogen unites with chlorine in the ratio of 12.6 to 443, with oxygen in the ratio of 12.6 to 100 and of 12.6 to 200.

Berzelius, one of the earliest chemists to draw up a set of

numbers, which cost him years of careful and arduous work in the analysis and synthesis of compounds, chose to take oxygen as his standard and to call it 100. Other chemists suggested hydrogen as standard, calling it unity, since it is the element that enters into combination in the smallest proportion, and for many years all the tables in the text-books had this standard. We can easily change the numbers given above to the new standard, it being only necessary to divide them all by 12.6, the number we had for hydrogen. The new numbers differ from the old, but they are in the same ratio to each other.

They are

Hydrogen	1
Oxygen	7.94
Lead	102.6
Chlorine	35.16
Sodium	22.87
Bromine	79.4
Potassium	38.8
Iodine	126

The number ordinarily used for oxygen is double that given above. Some of the most important reasons for this choice cannot be considered here, but one argument may be given which, though not entirely conclusive, has some weight. In water there is nearly eight times as much by weight of oxygen as of hydrogen. When water is acted on by sodium, one half only of the hydrogen is set free; the other half along with all of the oxygen unites with the sodium to form caustic soda. So the hydrogen of water can be divided into two parts, but there is no method known by which the oxygen of water can be divided. Any process by which oxygen is set free sets it all free; any element that takes away any of the oxygen takes it all away. It is therefore reasonable to consider water as made of *two* standard quantities of hydrogen and *one* standard

quantity of oxygen. Since *one* standard quantity of oxygen weighs nearly eight times as much as *two* standard quantities of hydrogen, *one* standard quantity of oxygen weighs nearly sixteen times as much as *one* standard weight of hydrogen. The number for oxygen is therefore doubled and becomes 15.88. In the same way the number for lead must be doubled. The number 15.88 is very nearly 16, and it is customary now to take oxygen as the standard and to call it 16. The table of numbers thus obtained is almost the same as with hydrogen taken as unity, but the numbers more frequently approximate whole numbers and are more convenient to use in calculations. Moreover, most of the numbers have been obtained by comparison with oxygen, since nearly all of the elements unite with oxygen and comparatively few with hydrogen. As the numbers are obtained by experiment, any experimental errors render them inaccurate. A large number of chemists have spent very many years in trying to eliminate errors, and almost every month a new determination is published of the number for some one of the elements. Each year a table is published by a committee who gather all the latest results. The changes in the numbers are but slight, usually in the second or third place of decimals, sometimes in the first place.

That a set of numbers for the elements could not be made if the law of reciprocal proportions were not true can be seen very clearly by consideration of a case where there is no law of reciprocal proportions. Alcohol mixes in all proportions with ether and also with water, but we cannot conclude that ether and water mix in all proportions. As a matter of fact, they mix very slightly; ether can dissolve only a very little water, and water can dissolve very little ether.

The fact that numbers can be obtained for the relative weights of different elements entering into combination lends support to the atomic hypothesis, but the *hypothesis* should be carefully distinguished from the *facts* upon which it is founded.

APPENDIX C

It is not necessary to introduce theory when fixing upon the best volume to take as standard for gases. Since hydrogen is the lightest gas, it is very natural to take as standard the volume of *one* gramme of hydrogen at atmospheric pressure and the temperature of freezing water. This volume is approximately 11.2 litres. But we find that though it may suit *some* gaseous *compounds* of hydrogen it is inconvenient for *others*. 11.2 litres of hydrogen sulphide contain one gramme of hydrogen; 11.2 litres of marsh gas contain two grammes of hydrogen; but 11.2 litres of hydrochloric acid contain half a gramme of hydrogen, and 11.2 litres of ammonia one and a half grammes of hydrogen. But all gaseous compounds of hydrogen occupying 22.4 litres (more exactly 22.412 litres) contain an exact number of grammes of hydrogen; hydrochloric and hydriodic acids, one gramme; hydrogen sulphide, two grammes; ammonia and phosphine, three grammes; marsh gas and ethylene, four grammes. Moreover, all gaseous compounds of nitrogen occupying 22.412 litres contain an exact multiple of 14 grammes, all gaseous compounds of oxygen an exact multiple of 16 grammes, all gaseous compounds of phosphorus an exact multiple of 31 grammes, all gaseous compounds of sulphur an exact multiple of 32 grammes; hence, 14, 16, 31, and 32 are the best numbers to represent the standard weight of these elements.

The formulæ we use for expressing the weight of gases may now be used to express the volume: NH_3 represents 17 grammes of ammonia, the volume of which at 0° C. and 760 mm. pressure is 22.412 litres; HCl represents 36.5 grammes of hydrochloric acid gas, the volume of which is also 22.412 litres.

Conversely, the weight in grammes of a gas occupying 22.412 litres gives the weight which the formula should represent, and when a new gas is discovered its formula is obtained by finding the relative weights of the constituents and by determining the weight contained in 22.412 litres. Suppose a compound of carbon and hydrogen just discovered is found to contain 80 % carbon and 20 % hydrogen, and suppose it is found that 22.412 litres of it weigh 30 grammes; it would follow that the weight of carbon is 24 grammes and the weight of hydrogen 6 grammes. Since all gaseous compounds of carbon have some multiple of 12 grammes in 22.412 litres, 12 is the standard weight of carbon and is represented by the symbol C, so that the formula of this compound of carbon and hydrogen would be C_2H_6.

The formula of elementary gases as well as of compounds is given by the weight contained in 22.412 litres; and since it is, for hydrogen two grammes, for nitrogen 28 grammes, for oxygen 32 grammes, the formula representing these gases is H_2, N_2, and O_2. The same volume contains 48 grammes of ozone, whose formula is therefore O_3.

It is evident how these considerations fixing upon the best standard volume for gases may be used along with the law of reciprocal proportions for determining the best set of numbers to represent the standard weights of elements.

APPENDIX D

ELECTROLYTIC DISSOCIATION

THE theory of electrolytic dissociation is not strictly a subject for discussion in a school-book on chemistry, but since references to it are frequent, it has been thought advisable to state briefly the prominent features of the hypothesis.

In order to get a clear understanding of the matter, it is necessary to consider a series of facts. As has been pointed out frequently the weight in grammes of a gas which at atmospheric pressure and 0° C. occupies the volume 22.412 litres is taken as the formula weight, and on the assumption of molecules and Avogadro's law the same number is used as the molecular weight. Thus 17 grammes of ammonia occupy 22.412 litres, and the formula NH_3 expresses this fact. Though water and ether and alcohol are not gases at the ordinary temperature and pressure, yet they can be volatilised and a calculation of the gaseous volume can be made. There are, however, a large number of substances which cannot be volatilised and whose formula weight cannot be obtained in this way, but many of them can be dissolved, and it has been discovered that some of them act in solution exactly as if they were changed into the gaseous condition. They exert a pressure somewhat similar to that of a gas. The pressure is not detected in the same way, but by a special contrivance, and it is called osmotic pressure.

One of the first substances with which experiments were made was cane sugar, and it was found that when 342 grammes of sugar were dissolved in 22.412 litres, the osmotic pressure

was equal to one atmosphere. The formula $C_{12}H_{22}O_{11}$ had previously been given to sugar, and the molecular weight, if this formula was correct, would be 342; therefore if sugar could be volatilised unchanged, 342 grammes at atmospheric pressure should occupy 22.412 litres. Many other substances whose molecular weight had been determined otherwise were found to act like sugar, and so from the osmotic pressure the molecular weight could be calculated.

The determination of osmotic pressure is difficult, and there are other methods more frequently used for the purpose of arriving at the molecular weight. Among these is the lowering of the freezing point. It is well known that when substances are dissolved in water the solution must be cooled to a lower temperature than is necessary for pure water in order that it may freeze. It was discovered that if the molecular weights in grammes of a number of different substances were dissolved in 22.412 litres of water, these different solutions would freeze at the same temperature, which was, as stated above, lower than the freezing point of pure water. Hence from the amount of lowering of the freezing point of water by the different substances in solution their molecular weight could be determined.

It was further found when what was considered to be the molecular weight of *some* substances, such as common salt, caustic soda, hydrochloric acid, nitric acid, was dissolved in 22.412 litres of water, that the osmotic pressure was nearly *twice* as much as was expected. So, too, the freezing point was lowered nearly *twice* the calculated amount. In 1887 Arrhenius pointed out that all of the substances that give higher values for osmotic pressure and that give a greater lowering of the freezing point are substances that in solution conduct electricity. Some of the substances can be dissolved not only in water but in other liquids, and often these latter solutions are found not to conduct electricity. In these cases it is also found that the osmotic pressure equals the calculated amount and is

not greater, as when the solution is made in water. So Arrhenius proposed the theory that in the solution in water the molecules are broken up or dissociated and that each part acts like a molecule. Thus the molecule of sodium chloride, NaCl, is dissociated into Na and Cl.

When sodium chloride is dissolved in water, none of the properties of sodium or of chlorine can be seen, but these properties appear if a current of electricity is passed through the solution, the sodium may be collected at the negative pole, and the chlorine at the positive pole. Since unlike electricities attract, it is a natural conclusion that the atoms are charged with electricity, sodium positively and chlorine negatively, and the electric charge on the atoms is considered to be what prevents the exhibition of the ordinary properties of the element.

Nearly all soluble salts and many bases and acids when dissolved in water are good conductors of electricity and have a greater osmotic pressure than substances like sugar, and these good electrolytes are considered to be largely dissociated.

It is now evident that electrolytic dissociation means the breaking up of the molecule into parts — one with a positive charge, the other negative. Since when a current of electricity is passed through the solution one part goes to one pole and the other part to the other pole, these parts are called "ions" from the Greek word which means "going," and the process of electrolytic dissociation is sometimes called ionisation.

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